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**A COURSE IN
COLLEGE CHEMISTRY**



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PREFACE

This book has been written for beginning college chemistry classes which are made up largely or entirely of nonchemists. The students in the writer's classes which use this book fall into two categories: nonscience majors who are taking a terminal course in the subject, and nonchemists who will take some additional work in chemistry, such as home economics majors.

The writer has attempted this book because he feels that the science of chemistry has now advanced so far, and the gap has become so great between the needs of preprofessional chemists and of those requiring only a limited knowledge of the subject, that a type of text different from those now available is necessary if we are going to recognize sincerely the best interests of the large group of nonchemists now taking chemistry courses.

The question of objectives in a beginning course for nonchemists is a controversial one. Some would limit it to a thorough study of the scientific method and not much else. Others teach chemists and nonchemists essentially the same. The writer feels that the first objective is too narrow in scope, while that implied in the second case is much too complicated and irrelevant for the nonchemist. In the present book the writer has tried to keep the following aims in mind: (*a*) to teach the nonchemist a little about the method of science, the periodic classification of the elements, and enough basic chemistry to be able, later, to (*b*) give the student at least an introduction to the chemistry of daily life, enabling him in some degree to avoid chemical blunders at home and at work, and to understand something of the fundamental chemistry of nature.

Some teachers would not attempt to go this far in a beginning course, but the writer feels that the average nonchemist among college students today likes to progress far enough to learn a

little about the chemistry of his own body, the plants in his garden, and the products of chemistry in his home. The writer believes, for example, that the nonchemist who knows that chlorophyll is green because it absorbs the other components of white light for use in photosynthesis will derive more satisfaction out of this understanding of nature than the nonchemist who was made to learn how we arrived at the molecular weight and structure of chlorophyll, but who didn't have time to get to the photosynthesis part.

The presentation of chemistry to nonchemists according to the writer's objectives requires a different organization than is usually found in general chemistry texts. The early part of the subject must be restricted to a discussion of the scientific method, the periodic system, and only those laws, theories, and facts necessary for a reasonable understanding of brief sections on the chemistry of daily life presented later. In the organization of topics, furthermore, it seems to the writer that the objective almost requires a progression based upon increasing molecular complexity rather than upon the periodic system, because of the necessity of treating heterogeneous systems such as the atmosphere as a unit, and because of the disproportionally large part played in everyday chemistry by the element carbon. It is with these thoughts in mind that the writer has attempted the present text.

Since chemistry is an experimental science, a desirable aim in writing a general chemistry text is to include a full description of the experimental basis for all statements. But with growth of the subject this has become increasingly difficult to accomplish, both because of the larger amount of experiment and because of its greater complexity. Today, with a rapidly expanding science but a fixed time for teaching it, the general chemistry textbook writer is forced more and more to condense his descriptions of experiments and to include statements which the student is asked to take pretty much on faith. This is even more the case in the teaching of nonchemists, not only for the reason just given, but also for the further reason that in order to include a fair

amount of the chemistry of daily life in the short time usually available in courses for nonchemists, the fundamentals must be presented with a minimum of background material. In the present book the writer has attempted to include as much experimental discussion as possible, consistent with the overall objectives.

A familiar problem in pedagogy, particularly in the smaller colleges, is that of teaching beginning chemistry classes which consist of a few chemistry majors and a much larger group of nonchemists. Such classes are frequently taught for the preprofessional chemists, while the nonchemist majority struggles along as best it can, often acquiring a distaste for the subject which is voiced in later years.

The writer would like to suggest as an alternative in such classes the use of a text which is interesting and understandable to the nonchemist majority, plus the assigning of additional work to the chemists from one or more of the excellent texts now available for that group. With supplementary work, a textbook for nonchemists need not be unsatisfactory for chemistry majors, and in this connection the writer would like to report that a number of chemistry graduate students, not his own, have come, unsolicited, during the past several years and borrowed the duplicated manuscript which the writer has been using in his courses for nonchemists, and upon which this book is based. As one student put it, he had been looking at the trees so long, these lecture notes helped him to see the woods.

The writer wishes to express his deep gratitude to the several dozen experts who have assisted him in the preparation of this text, and particularly to Dr. Calvin Vander Werf of the University of Kansas, Dr. John Martens of the U. S. Atomic Energy Commission, and colleague Dr. Franklin Bacon, who have been of great help in important sections of the book. The author has endeavored to write a book that is free from errors, obsolete material or significant omissions, but takes full responsibility for any of these shortcomings if they should come to light, and in that event he will greatly appreciate it if such will be reported to him.

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INTRODUCTION

Chemistry as a Science

First Definition of Chemistry. Chemistry is a science which deals largely with atoms and molecules, and with their combinations and separations during the formation of different kinds of material substances. Today, beginning chemistry students with even the most meager scientific background have heard or read enough about the words "science," "atom," and "molecule" to grasp pretty well the meaning of this first definition. But to insure better understanding, both of this and of the fuller statement of the scope and objectives of chemistry which will shortly be given, these three terms will be discussed in some detail.

Science. In its simplest sense, a science is an organized body of knowledge. This involves first the systematic arrangement of facts. If a button collector, for example, were to classify the thousands of buttons in his possession according to source, age,

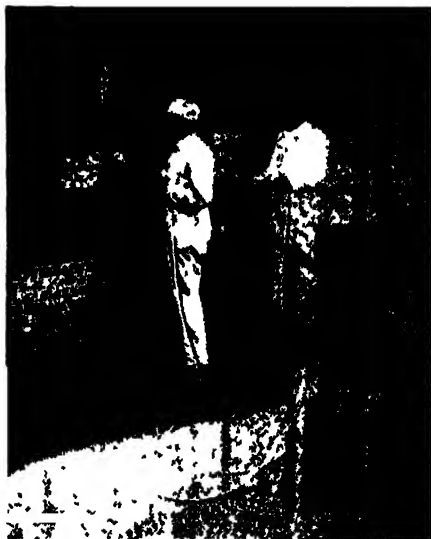


FIGURE 0.1. Chemistry Deals with Molecular Changes. In the scene depicted molecular changes are taking place during the deterioration of paint, the burning of acetylene, the setting of paint, the growth and maintenance of life in plants and human beings, the corrosion of metal, the aging of insulation, wood, leather, felt, clothing, mortar, and concrete. Courtesy The Linde Air Products Company.

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shape, probable value, number of holes, etc., he would be taking the initial step toward making his hobby approach the status of a science. Classification is not synonymous with organization, however, since the latter term also implies the presence of interrelationships and unifying entities which are not apparent in a mere classification. The interrelationships and unifying entities in a button collection would be so few and so obvious that this hobby would probably be considered too simple to develop into a science.

A number of important and complex fields of learning do exist, however, which can advantageously be organized as sciences. Among the basic ones are those dealing with various aspects of nature, and these are in fact the chief bodies of knowledge to which the word science is applied. They may be concerned with inanimate nature, as the sciences of geology or astronomy, or they may have to do with life, as the biological sciences of botany and zoology.

The Method of Science. In these big, important sciences there is more than merely the accumulation and classification of facts. A procedure known as the *scientific method* is employed as an aid to organization, growth, and the finding of objective truths. By the scientific method is meant, briefly, the gathering of data as the result of experiment and observation, the finding of general types of behaviour from this, called *scientific laws*,¹ the thinking out of possible explanations for these laws, which go under the name of *hypotheses* or in more complete form, *theories*, and the devising of new experiments to test these and determine their correctness. Additional facts resulting from these experiments lead to additional laws, theories, and experiments, and

¹ However, scientific laws as we state them are actually only man's clumsy attempts to summarize the highly complex behaviour of nature. As experimental measurements are made under more and more extreme conditions, such laws are often found to require larger and larger corrections to make them consistent with fact, and even under the most favorable conditions careful experimental work sometimes reveals small differences between observed results and those predicted by a scientific law. Read, for example, of the failure of the gas laws under certain conditions, on pages 57 and 102.

the process continues, not as simply as indicated, but along these basic lines. When the scientific method is used, then, a science does not remain static, but becomes an ever-increasing body of facts, laws, and theories. And with each advance the horizon not only changes, but also appears to become wider.

The reader may imagine that the scientific method is something which is used only by a few scientists at the frontiers of their fields of specialization. While this may have been true long ago, the scientific method today is employed, not only throughout the natural sciences, but also in such places as industry, agriculture, the waging of warfare, and even in the home, as the frame of mind which characterizes the method permeates throughout all society.

The beginning chemistry student might not yet be sufficiently familiar with the subject to understand at this time an example of the scientific method as used in chemistry, but as a simple illustration of how it might be used in daily life, consider the following: A man could look at his lawn during an August dry spell and note that, while the grass was brown, the dandelion plants remained green. He might conclude from this that the roots of the dandelions must be longer, and reach deeper into the ground than the grass roots, to obtain enough water to keep the plants green. If he had never seen dandelion roots, and knew nothing of their shape or length, he would be formulating a *hypothetical* explanation of the observed phenomenon. If, on the other hand, he was recalling what he had already been told, or had read, or seen, he would merely be using his memory, and this would not be an example of the scientific method. Some time later, if the ground became sufficiently soft after a rain, he might pull up the dandelions and *observe* that each had a long root, thus testing his theory by experiment according to the method of science. A summary of fact could then be made based upon the examination of many plants: *Dandelions have long roots*, and if this were important enough it could be called a scientific law. He would have gone through the cycle which often characterizes the scientific method.

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- A. Observation leading to scientific law
Dandelions stay green in dry weather longer than grass
- B. Theory to explain law
Dandelions must have long roots in order to reach water during dry weather
- C. Experiment to test theory
Pull up dandelions and observe roots
- D. Conclusion
Dandelions do have long roots; theory is correct
- A. Observation leading to scientific law
Dandelions have long roots, etc.

This process of using the mind to devise an explanation for some phenomenon (proposing a theory) followed by the carrying out of experiments which show the imagined state of affairs to be correct or incorrect occurs continually in science. It is the backbone of the scientific method.

Insight into the working of nature is only one of the advantages gained by the use of scientific theory. A further advantage is that predictions can be made, and future events can be planned or anticipated, e.g., the man who first theorized that rain came from clouds had a better chance of staying dry than his neighbor in the next cave who had never connected the two. The ability to establish scientific laws and theories and to think ahead in terms of these is one of the great differences between men and animals.

A significant gain will be made if the method of science can become sufficiently well known among the people of the world to influence their thinking in daily life. This will be true not only from the standpoint of technological advances, but in other ways as well, as for example in their attitude toward their leaders. They will begin to judge the opinions (hypotheses) of persons in the public eye on the basis of reason rather than emotionally. The statements and writings of advertisers, politicians and demagogues will be treated as unproven hypotheses. Their pronouncements will be accepted or rejected, by people who understand and apply the scientific method, only after a

study of the facts, and better living and better government will be the result.

Atoms and Molecules. To make the first definition of chemistry more clear the following preliminary discussion of atoms and molecules is included. This topic is also considered in greater detail in the next chapter.

As the result of a great mass of experimental evidence, scientists have reached the conclusion that all material substances consist of atoms, and that these in turn are usually joined together into larger units known as molecules.² Both atoms and average sized molecules are exceedingly small objects. To illustrate this point let us consider a single drop of pure grain alcohol. This substance will contain atoms of carbon, hydrogen, and oxygen. If we assume our drop to weigh 0.04 gram (slightly over one thousandth of an ounce), there will be present approximately one sextillion³ carbon atoms, three sextillion hydrogen atoms, and 0.5 sextillion oxygen atoms, which gives the reader some idea of the size of atoms.

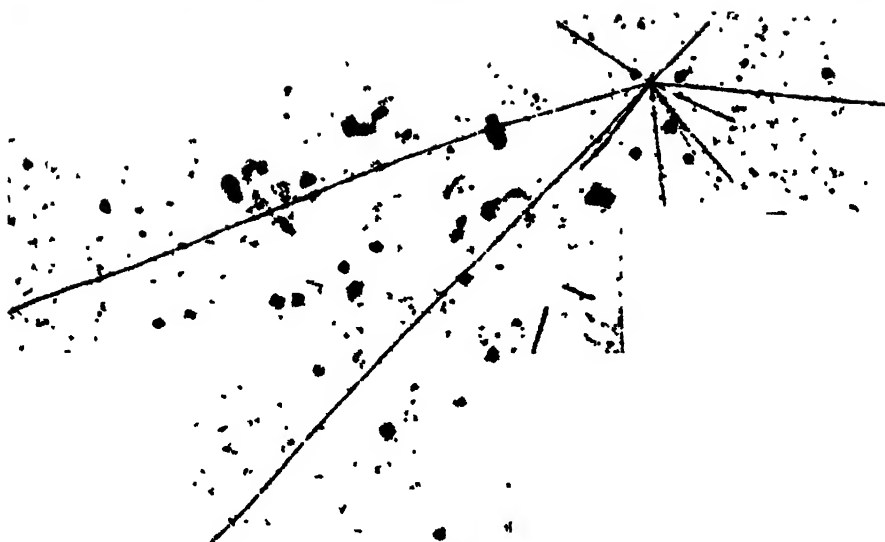
But it is not only the presence of carbon, hydrogen, and oxygen atoms which makes this particular liquid grain alcohol. These atoms are joined together in a certain characteristic manner to form larger units known as *alcohol molecules*, each of which contains two carbon atoms, six hydrogen atoms, and one oxygen atom. The composition and structure of these larger units gives this particular liquid the appearance, odor, taste, viscosity, density, and all the other properties which make it grain alcohol and not something else. Thousands of other substances containing carbon, hydrogen, and oxygen are known, such as ether, sugar, and acetic acid (which accounts for the sour taste of vinegar). It is the specific manner in which the

² Evidence for the particulate structure of matter: Brownian movement (page 46), fog tracks in cloud chamber experiments (page 291), constancy of composition of isotopically similar pure substances, spreading of odors, gas pressure, change of gas pressure with volume, mass spectrograph data, Geiger counter data, and much more.

³ One sextillion - 1,000,000,000,000,000,000.



(a)



(b)

FIGURE 0.2 Evidence for the Particulate Structure of Matter. (a) Fog tracks produced by disintegrating carbon and oxygen atoms in the 184 inch cyclotron. Curvature is due to movements of charged particles in a magnetic field. Courtesy University of California Radiation Laboratory. **(b)** Result of cosmic particle striking a photographic plate 17 miles above the earth. Courtesy Eastman Kodak Company.

atoms are combined into molecules which distinguishes each of these compounds.

Place of Chemistry in the Natural Sciences. Mathematics, physics, and chemistry are generally regarded as the basic sciences, knowledge of which is necessary for the most complete understanding of the remaining natural sciences. Mathematics is required in all quantitative research or exact theory. Physics, dealing chiefly with energy in such forms as light, heat, and electricity, and chemistry, concerned with the atomic and molecular nature of matter, are both needed in such sciences as biology, astronomy, or geology, since various aspects of both matter and energy are studied therein.

The science of physics also deals to some extent with matter, in connection with such concepts as gravity, momentum, and acceleration, and too, chemistry must occasionally be concerned with energy, as when heat is liberated during a chemical reaction. The borderline between these two fundamental sciences is therefore not sharply defined, and there is some overlapping. Indeed, as all of our sciences grow, their areas of knowledge appear to overlap more and more, leading to such joint sciences as geophysics, biochemistry, physical chemistry, etc. Some of our most striking scientific advances occur in these joint fields.⁴

Scope of Chemistry. Chemistry is concerned in part with the composition of matter, not in terms of large, visible units, but on the basis of the atoms and molecules present. The fact that a box is made of wood and nails or a wall of bricks and mortar is not of primary interest to the chemist. He thinks of the wood as being composed of cellulose and lignin molecules, and the nails as aggregates of iron atoms. The bricks in a wall, likewise, are regarded as mixtures containing kaolin and iron oxide, and the mortar as silica, calcium carbonate, and calcium hydroxide.

Chemistry is also vitally concerned with *changes* in the compo-

⁴ Production of antibiotics, vitamins, and other substances by the methods of biochemistry; finding of uranium and petroleum deposits by geophysical methods; distilling petroleum according to the theory of physical chemistry, etc.

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sition of matter, as when one kind of molecule decomposes to form other, simpler kinds, or reacts with others to form more complicated kinds. Here again the chemist thinks of these changes in terms of atoms and molecules. In the burning of paper, for example, he pictures the cellulose molecules which make up that material as reacting with certain air molecules (oxygen) to form molecules of carbon dioxide gas and water vapor.

While chemistry deals chiefly with composition and changes in composition of matter, it is not limited to only these objectives. Thus, the chemist measures the energy absorbed or released when chemical changes occur, and draws valuable conclusions from this data. He is also interested in the properties of matter, such as color, melting and boiling temperatures, ductility, density, etc. He is concerned with the procedures used to detect various substances (qualitative analysis) and with methods used in establishing purity and percentage composition (quantitative analysis). Chemistry deals with so many different aspects of matter that a short, simple statement of its scope is not possible.

These, then, are the chief objectives in chemistry:

1. *To Learn the Atomic and Molecular Composition of Material Substances.* The composition of the substances in the atmosphere, of hundreds of minerals in the earth's crust and of many thousands of compounds of carbon are among those now known.

2. *To Learn the Changes Which Occur in the Composition of Matter.* Besides learning about many changes which take place during such processes as burning, corrosion, or neutralization, we are also beginning to understand more complicated changes such as those occurring in plants and animals during respiration, digestion of food, fermentation, etc.

3. *To Learn to Duplicate by the Best Possible Methods the Molecules Found in Nature.* Chemists can now synthesize, at a cost less than that of recovery from natural sources, such widely divergent products as dyes (such as indigo), acids (such as the acetic acid of vinegar), vitamins (such as thiamin), antibiotics (such as chloromycetin), gems (such as sapphire), perfumes (such as ionone, which has the odor of violets), etc.

4. *To Learn How to Make New Molecules Out of Existing Kinds by the Best Possible Methods.* A large number of new kinds of molecules have

been made by the chemist, many having properties which make them of value, as for example new resins for plastics and fibers, synthetic rubber, sulfa drugs, adhesives, lubricants, detergents, etc.

5. *To Learn of the Energy Released or Absorbed as Chemical Changes Take Place.* The determination of the fuel value of different kinds of coal is an example of this chemical objective.

6. *To Learn to Detect and to Quantitatively Estimate Chemical Substances.* Thousands of methods are employed by the chemist for qualitative and quantitative analysis. Exceedingly small traces of substances can now be determined, such as 0.00001 per cent of lead or arsenic in food and other materials.

7. *To Learn the Properties and Uses of Substances.* Large numbers of chemists and other scientists are at work learning the properties of, and searching for uses for, different, and particularly new, kinds of chemical substances, such as synthetic resins, biochemicals, alloys, insecticides, solvents, catalysts, etc.

8. *To Learn the Reasons for All Phenomena Observed.* As we better understand Nature, so can we more effectively predict and control events of the future.

MATHEMATICAL REVIEW; UNITS OF MEASUREMENT

General chemistry occasionally requires use of simple mathematics. In the next few pages the subject is reviewed for the benefit of those who feel they need it.

Direct Proportion. A working knowledge of direct proportion is required in many chemical calculations. Consider the following process, similar in some respects to a chemical change.

There is a pile of bolts and a pile of nuts. A workman is screwing two nuts on each bolt and making a third pile out of the resulting combinations. If a chemist could be induced to think of nuts, bolts, and combinations as he does about atoms and molecules, he might write an equation:

2 nuts and 1 bolt form 1 combination

However, if he followed the chemical custom he would use abbreviations for the words "nut" and "bolt," and for the words "and"

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and "form" he would use a plus sign and an arrow. He would also show the number of nuts and bolts in each combination. Thus:



Nu_2Bo of course means two nuts and a bolt fastened together. Finally he would omit the 1 as being unnecessary; the absence of a digit would mean that 1 was understood.

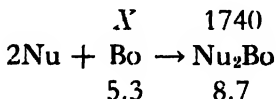


Observe that the sum of the units on the left (3) does not equal the number on the right (1) because the right-hand unit is larger, and therefore fewer of them are formed. The same thing is often true when atoms and molecules react.

Now let us imagine each nut to weigh 1.7 grams and each bolt to weigh 5.3 grams, whereupon each combination would weigh 8.7 grams.⁵ The problem might arise: What weight of bolts will be needed to form 1740 grams of Nu_2Bo combinations? Since a 5.3-gram bolt is present in an 8.7-gram combination, the direct proportion can be written:

$$\frac{\text{X grams of bolt, required}}{5.3} = \frac{1740}{8.7}$$

and X comes out to be 1060 grams. A common procedure in chemistry is to form such proportions around the equation involved, putting the standard masses below the things to which they apply and the numbers in the problem (X and 1740, here) above.



⁵ This is assuming that no mass (page 23) change occurs when a combination is made from individual nuts and bolts, as can readily be verified with a balance. The same constancy of mass was observed long ago (Lavoisier, 1785) in the case of combining atoms and molecules. The *Law of Conservation of Mass* summarizes the conclusions from the experimental work done. *The total mass of the materials in any system remains constant, regardless of what physical or chemical changes occur within that system.* Recent work, however, indicates that radiation (page 54) must be included as one of the components contributing to mass in such systems.

The direct proportion is then made from these four quantities, keeping each in its same relative position. Use of this procedure helps in the setting up of such proportions correctly. However, devices like this should not be employed merely as shallow memory aids which discourage thinking.

Inverse Proportion. Another type of calculation sometimes used in general chemistry is the *inverse* proportion. Thus, if workman A takes 10 seconds to make a combination of nuts and bolts and workman B requires 15 seconds, how many combinations will B put together while A is making 600 combinations?

The number made at the end of any given time will be inversely proportional to the time required to make a single combination, or

$$\frac{\text{A's time for one comb.}}{\text{B's time for one comb.}} = \frac{\text{Number made in time } T \text{ by B}}{\text{Number made in time } T \text{ by A}}$$

or

$$\begin{aligned}\frac{10}{15} &= \frac{X}{600} \\ X &= 400\end{aligned}$$

Exponents. In this book the number ten with a positive or negative exponent will occasionally be used. 10^2 is 10×10 or 100, 10^3 is 1000, and 10^6 is 1,000,000, and in general 10^n will be the digit 1 with n zeros after it. The number 2,136,000 can then be written 2.136×10^6 , etc. Negative exponents may also be used, with the understanding that the reciprocal of the number with the corresponding positive exponent is intended. Thus, 10^{-3} means $1/10^3$, or $1/1000$, or 0.001. When ten with a negative exponent is used, therefore, it means the number one with the decimal point moved as many places to the left as the numerical value of the exponent. Hence, 10^{-7} means 0.0000001, and by using 10^{-7} we have avoided writing many extra zeros. In the same way, the mass of a tiny atom of hydrogen, which is 0.0000000000000000000000017 gram, can be written more simply as 1.7×10^{-21} g.

One advantage of using the number ten with positive and

negative exponents is that excessive writing of zeros is avoided. Another advantage is that the part of the quantity actually measured or calculated from actual measurements can be shown in the left-hand part of the expression, while the right-hand portion serves merely to locate the decimal point. In this way we are able to indicate in the written expression the accuracy with which the experimental measurements were carried out, whereas writing it the other way may lead to some confusion on this point, particularly if the last experimentally determined digit to the right happens to be a zero.

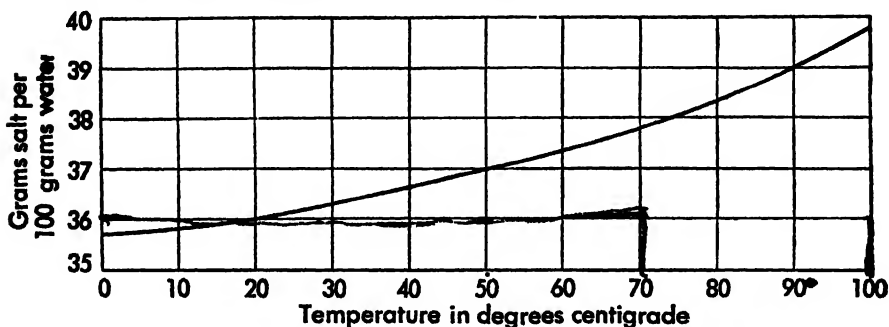
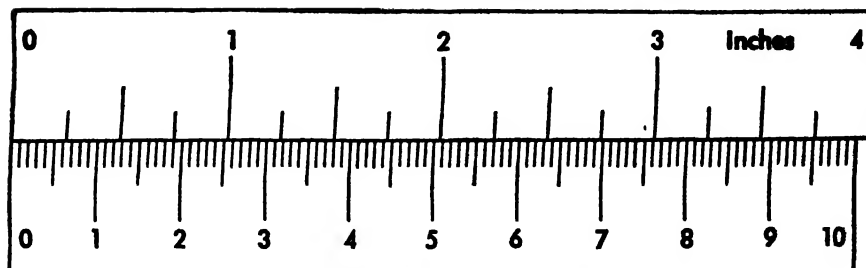


FIGURE 0.3. Solubility of Sodium Chloride in Water at Various Temperatures.

Graphs. The reader should understand graphs. Consider the one in Figure 0.3 which gives the change in solubility of table salt in water as the temperature is increased. This shows, for example, that 35.7 grams of salt will dissolve in 100 grams of water at 0°C., 37.0 grams at 50°C., and 39.8 grams at 100°C.

Units of Measurement. Finally, the reader should be prepared to see quantities expressed in the units of the scientists, rather than in those employed in the home, because of their greater ease of conversion from one size to another (often related by a power of ten), and their international usage.

The meter is the primary standard of length, originally intended to be one ten-millionth of the distance from the equator to the North Pole. It is a little over a yard, or 39.37 inches. Sub-divisions of this unit used in chemistry are shown on the next page.



100 millimeters = 10 centimeters

FIGURE 0.4. Relation between Inches and Centimeters.

<i>Length unit</i>	<i>Remarks</i>
CENTIMETER	0.01 meter
MILLIMETER	0.1 centimeter The limit of resolution of the human eye is about 0.15 mm.
MICRON	0.001 millimeter The limit of resolution of the microscope is about 0.2 micron in ordinary light and about 0.1 micron in ultraviolet light.
MILLIMICRON	0.001 micron The limit of resolution of the electron microscope is a small number of millimicrons. The limit of visibility in the ultramicroscope is about 2 millimicrons.
ÅNGSTRÖM	0.1 millimicron or 10^{-8} centimeter This unit is used in expressing atomic and molecular sizes.

The primary standard of mass is a piece of metal—a platinum iridium alloy—kept in Paris and duplicated as carefully as possible in other places. The mass of this alloy is called a *kilogram*, 2.205 pounds. This is too large a unit for most chemical work, and the following subdivisions are used.

<i>Mass unit</i>	<i>Remarks</i>
GRAM	0.001 kilogram
MILLIGRAM	0.001 gram Weighing on an ordinary analytical balance is not usually carried out below 0.1 milligram.

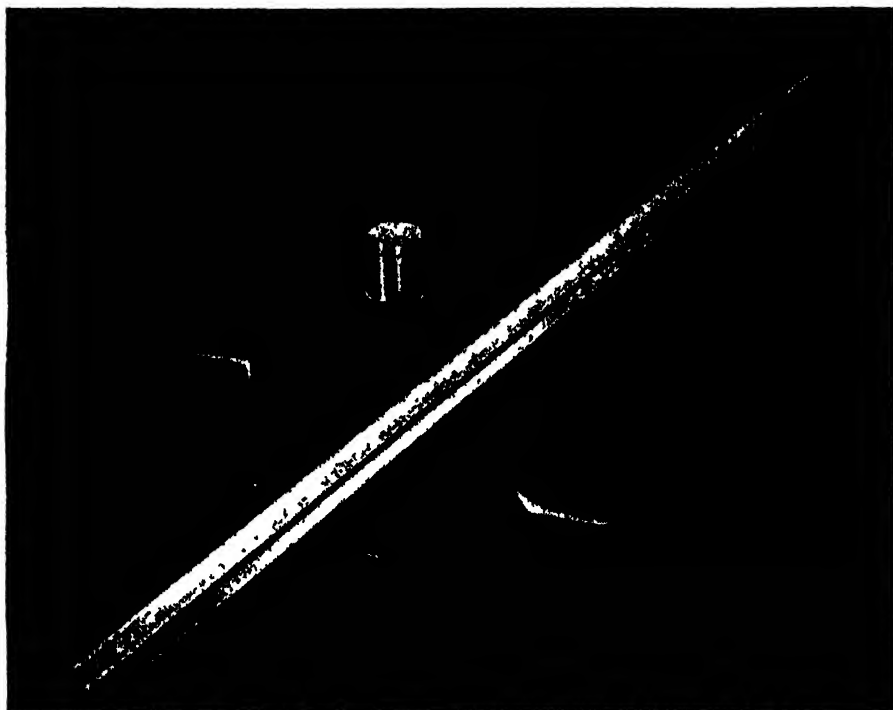


FIGURE 0.5. Mass and Length Standards. A platinum-iridium cylinder at the National Bureau of Standards is the standard kilogram, defining all metric measurements of mass in the United States. Comparison with the international standard has shown that the United States standard changed only one part in fifty million in approximately fifty years. The standard of mass, 39 millimeters high and 39 millimeters in diameter, is made of an alloy containing 90 per cent platinum and 10 per cent iridium.

The distance between two parallel lines engraved on this platinum-iridium bar kept at the National Bureau of Standards is the primary standard meter for all metric measurements of length in the United States. The meter bar is made of an alloy containing 90 per cent platinum and 10 per cent iridium.

The national standards of mass and length, far from being just inert objects deposited in a vault at the National Bureau of Standards for safekeeping, function actively as fundamental references and controls in commerce and industry. Laboratory and industrial weights are checked against "working standards" of mass, which in turn are compared at intervals with the standard kilogram. Likewise laboratory and industrial measuring bars and tapes are checked against "working standards" of length, which are compared at intervals with the standard meter.

Courtesy National Bureau of Standards.

Mass unit
MICROGRAM OR GAMMA

0.001 milligram

Weighing in microanalysis is not usually carried out below one microgram.

AVOGRAM

Unit of atomic mass recently adopted by the American Chemical Society.⁶ An avogram is 1.660×10^{-24} gram. The reason for making the unit this particular fraction of a gram will be discussed later (page 104).

The scientific unit of volume is the liter, about 1.06 quarts. It is the volume occupied by a kilogram of water at 4°C. There are two smaller units of volume in common use. One is the milliliter, exactly one thousandth of a liter. The other is the cubic centimeter, essentially the same, but because of an early experimental error it is 0.00099997 liter. The two volumes are considered the same for most purposes, and both are widely used in scientific work.

The Centigrade temperature scale is employed in most scientific work, on which water freezes at 0°C. and boils at 100°C. under one atmosphere of pressure. Quite different from this is the Fahrenheit scale, on which water freezes at 32°F. and boils at 212°F. To convert the Fahrenheit temperatures used in the home to the corresponding Centigrade temperatures it is necessary to subtract 32 and multiply the re-

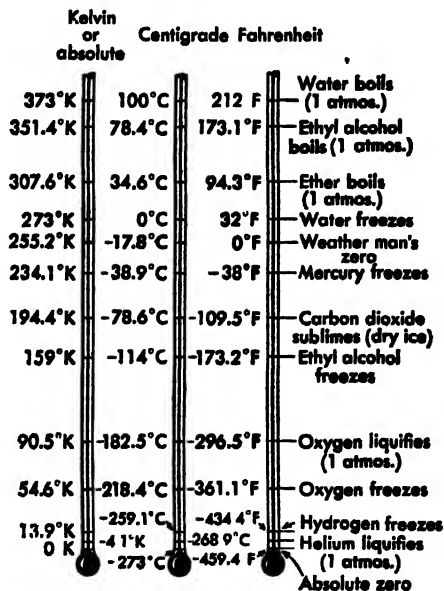


FIGURE 0.6. Comparison of Temperature Scales. Although the tube markings are shown extending to absolute zero, actually this type of thermometer cannot be used to measure very low or very high temperatures.

maintaining quantity by the fraction $\frac{5}{9}$. Thus, 50°F. becomes 10°C. , i.e., $(50 - 32)(\frac{5}{9}) = 10$. Conversely, a Centigrade temperature must of course be multiplied by $\frac{9}{5}$, and 32 added to the product, to convert it to the corresponding Fahrenheit reading.

For very low and very high temperatures, as in describing stellar temperatures, and also for research with gases, another scientific temperature scale is used, the Absolute or Kelvin scale. Here, water freezes at 273°K. and boils at 373°K. , under one atmosphere of pressure. Absolute temperatures are obtained from the corresponding Centigrade temperatures by adding 273. Thus, 25°C. is 298°K. , while 500°K. is 227°C.

Problems dealing with graphs, exponents, and units of measurement are given in the chapter on supplementary problems (Chapter XXVI) and in the Self Study Questions at the end of this chapter.

LEARNING CHEMISTRY

The Learning Process. Learning chemistry, or anything else, is chiefly a memory process (unless it be by trial and error). To a considerable extent this must be the learning of facts, e.g., the symbol for potassium is K, the valence of magnesium is two. But besides the committing to memory of things expressed with words (theories, laws, individual facts), a few mathematical procedures will have to be known if the student is going to carry out calculations. This is somewhat different because it involves the placing of numbers in certain positions, as in the setting up of direct or inverse proportions, or in multiplication or division.

The learning of college chemistry should involve more than merely a parrot-like memorization of facts, laws, theories, and mathematical procedures, however. In situations such as the solving of a problem, or in deciding on the theory which explains a certain fact, the student must make up his mind *which* mathematical procedure or *which* theory applies to the question. To do this, the process of *thinking* is required, in which the nature of the question or problem is carefully considered in terms of the theories or mathematical procedures available. Even here much

use of the memory is required, as in the recall of basic relationships, or of similar problems, and how they were solved. Thinking is so closely tied up with the memory that the accuracy and scope of the former depends pretty much upon that of the latter.

Learning Aids. The student should strive to learn as efficiently and as accurately as possible. Following are some aids to fast, precise learning.

Interest in things, and the recognition of their importance are of prime significance in determining the rate and accuracy of learning, i.e., we *remember* things which impress themselves at the time as being interesting and important. The chemistry major has of course no difficulty in accepting the significance of chemistry, and if the nonchemist reader will realize that he will be better able to avoid chemical blunders in the home and at work and that he will derive personal satisfaction and a certain amount of prestige for the rest of his life by knowing the chemical basis for the things which go on about him in his daily life, he, too, will more readily learn chemistry.⁷ When the reader really believes, subconsciously, that something to be learned is important to him, he will be able to concentrate, and learning can then become very rapid indeed.

Organization is also a great aid to learning. Any device by which one key thought automatically leads to several others insures better learning than trying to memorize information about the same things as separate, unrelated items. Thus, as a student of organic chemistry the writer learned the first seven dibasic organic acids by making the word "omsgaps" out of their first letters⁸ and learning that. The names of the acids then came automatically to mind, and in their proper order. Devices

⁷ In addition to the specific advantages of chemistry itself, chemist and non-chemist alike profit in another way from the sincere study of this, as of any other natural science, because all teach one of such things as the beauty often found while making careful observations, the accuracy gained during the meticulous collecting of data, the honesty involved in reporting it, the courage with which one should uphold convictions based upon sound facts and the tolerance necessary for the facts and opinions (hypotheses) of others.

⁸ Oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic acids.

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of this sort are not really necessary, of course, since material is learned systematically, and more easily recalled, merely by keeping in mind the overall organization used in describing it.

Laboratory experiments, and the observation of chemical changes taking place in the home and elsewhere, help greatly in the learning process. Thus, actually seeing the evolution of hydrogen when zinc and hydrochloric acid react, for example, creates a much greater impression upon the mind than reading about the same thing in a book, and smelling the product of a hydrogen sulfide generator teaches everyone at once, and rather permanently, that this substance has an objectionable odor.

Writing things down helps in learning, as does repetition; both of these can be practiced by the construction of a learning pack—a series of small pieces of paper, as from a scratch pad, with things to be learned on one side and the answers on the other. The reader will be amazed at the speed with which he can learn when he constructs such a pack and goes through it alertly several times.

Finally, it is important that material be learned accurately *at the start*. Incorrectly learned things which are later corrected set up a state of confusion in the mind which is difficult to dispel.

These points apply not only to chemistry, but to college work in general, and beyond that to learning in general, which the reader will be doing the rest of his life.

Self Study Questions

1. Name five bodies of knowledge, not directly connected with nature, which could be organized as sciences.
2. Describe what is meant by the scientific method. Distinguish between a scientific law and a theory.
3. What are the chief objectives in the science of chemistry?
4. Write the distance from the earth to the sun (93 million miles) with a power of ten. Write the quantity 1.37×10^{-13} without a power of ten.

5. What are the chief scientific units of length, mass, volume, and temperature?

6. How many millimeters are in a meter? How many angstroms are in a centimeter? How many avograms are in a kilogram?

7. Convert 72°F. to the corresponding Centigrade temperature. Do the same with body temperature (98.6°F.). What Fahrenheit temperature will correspond to 200°C. ? To 1000°K. ?

Answers: 22.2°C. , 37°C. , 392°F. , 1340.6°F.

8. What weight of salt can be dissolved by 100 grams of water at a room temperature of 70°F. ? What weight of salt can be dissolved at this temperature by a quart of water (944 grams)? How many ounces will this be, if there are 28 grams to the ounce?

Answers: 36 g., 340 g., 12.1 oz.

9. 500 grams of boiling water, at 100°C. , is saturated with salt. The solution is then cooled to 25°C. How much salt will separate out?

Answer: 18.0 g.

10. Describe four practices which will lead to faster, more accurate and more permanent learning

11. Can you carry the illustration of use of the scientific method on page 4 any further by proposing another hypothesis and additional experiments to test it?

12. Give further examples of how the scientific method could be employed in the home, as in cooking, gardening, etc.



PART ONE

The Atmosphere

I

Composition and Structure

Matter and Its Complexity. The science of chemistry is chiefly concerned with *matter*. We mean by this term anything in the universe which has mass.¹ The earth, the sun, and other stellar bodies are examples of matter on a large scale. The surface objects on the earth – trees, buildings, people— are smaller aggregates of matter.

Chemists have found after the examination of a great many kinds of matter that there is a very considerable range in its complexity. That found in solids, e.g., earth or wood, is generally the most complicated in structure, particularly in solids based upon the element carbon. The matter in liquids, such as water or alcohol, is of intermediate complexity, while that which makes up gases is the simplest.

These latter substances are then the proper ones to study at the beginning of a first course in chemistry. There are a number of gases, but the reader is most interested in those he meets in his daily life, and particularly in the mixture of gases in which he spends his entire life— the air or atmosphere. Let us hence make this the first variety of matter which we study in chemistry.

Composition of the Air. This huge blanket of colorless gases, whose presence is usually not noticed except when it is in motion relative to the observer, appears to be homogeneous, i.e., all

¹ That property of matter which determines its inertia, or resistance to a force tending to cause a change in the state of motion. The *weight* of an object, on the other hand, is determined by the gravitational pull of the earth. Weight is variable, becoming less as the distance from the earth's center increases, whereas the *mass* of an object is constant.

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parts of it seem to be alike. But when analyzed it is found to consist of many different components, as shown in Table 1.1.

TABLE 1.1 Composition of the Air at the Earth's Surface

<i>Component</i>	Molecules per 10,000 Air Molecules		
	<i>Relatively dry air</i>	<i>Average air</i>	<i>Humid air</i>
NITROGEN	7795	7725	7413
OXYGEN	2097	2078	1994
ARGON	94	93	89
WATER VAPOR	10*	100*	500*
CARBON DIOXIDE	3*	3*	3*
HYDROGEN	1	1	1
NEON			
HELIUM			
KRYPTON			
XENON			

* The water content is of course variable, even for each type of air. Thus, air containing 400 or 450 molecules of water vapor per 10,000 air molecules would also be classed as highly humid at ordinary temperatures. The carbon dioxide content of the air is also quite variable. The 3 molecules in 10,000 is an average value.

Nearly four-fifths of the air is seen to consist of *nitrogen*. The structure of the atoms which make up this gas will now be considered, and used in the explanation of some terms and ideas fundamental to chemistry.

✓ THE NITROGEN ATOM

If one were able to subdivide a sample of nitrogen over and over again, there would come a stage far along in this process in which the smallest unit possible to exist would remain—a nitrogen atom. The reader cannot properly appreciate the tininess of this object when we say its radius averages—from several different methods of calculation—in the neighborhood of an angstrom. A better visualization of its size can be had by considering the following process. Let the reader imagine himself shrinking in height 2000 times, to the size of a small insect, then 2000 times again, to the size of a bacterium, and finally 2000 times once more. This imaginary three-stage process would

make an average person a little over 2 angstroms tall, approximately the size of a nitrogen atom.

General Acceptance of the Existence of Atoms. No one has / seen a nitrogen atom, but the evidence for its existence is nevertheless so overwhelming that few, if any, scientists doubt its occurrence, or the occurrence of other kinds of atoms. The existence of atoms as the building units of matter was proposed as a theory by the Greek philosopher Anaxagoras some 2400 years ago, and again by Dalton, in a much more accurate and acceptable theory, in 1803. Today their presence is accepted as fact rather than theory, and a large amount of data on their properties and structure has been accumulated.

Atomic Structure. We know the atom is the smallest unit of nitrogen that can exist, because if it is further subdivided we get subatomic particles whose properties are very different from those of nitrogen. These parts of atoms, *by themselves*, are perhaps of greater interest to physicists and the nuclear scientists than to most chemists, but *as parts of an atom*, they are of great importance to chemists, too, because the properties and behaviour of atoms can be more clearly understood if we know something of their structure.

In the early days of science nothing was known of the composition of atoms. If this was thought of at all they were probably imagined as little spheres, perhaps something like marbles. Today we have a partial knowledge of the structure of atoms, enough to make us intensely curious to learn more. We know at least the major components of an atom, the mass of these, something of their size, and have some idea of how they are arranged within the atom. Our knowledge comes chiefly from experiments in which portions of atoms have been knocked out by bombardment with various subatomic particles (Chapter XII). We have also learned much about internal structure by studying the radiation (page 54) which is given off when atoms are heated. The detailed experimental evidence for our findings is beyond the scope of this book, so without further reference to it let us consider what we believe to be the structure of the nitrogen atom.

Outer Structure of the Nitrogen Atom. The evidence indicates that the outer part of a neutral (uncharged) nitrogen atom consists of five electrons which move in paths known as orbitals. Farther within the atom are two more electrons with smaller orbitals. These electrons are tiny bits of electricity, the smallest we believe can exist. Electrons are also known in the free state, unassociated with any specific atoms, and in this form they constitute electricity, familiar to all in the controlled state in the home and in the uncontrolled state as lightning. Electrons are known to possess a negative charge, because of the manner in which they behave in a magnetic field. The nitrogen atom therefore consists in part of seven negatively charged units of electricity.

The Nitrogen Nucleus. In the center of the nitrogen atom is an exceedingly small part known as the nucleus (plural, nuclei). To give the reader an idea of the size of a nucleus, as calculated from collision data, let him imagine that our nitrogen atom can be expanded in some miraculous manner to the size of a twenty-story building covering a whole city block. The nucleus, similarly expanded, would now have the volume of a small marble, according to our generally accepted calculations. Furthermore, scientists have reached the bewildering conclusion that in spite of its size, tiny even when compared to an atom, the nucleus contains almost all of the mass of the nitrogen atom, about 99.97 per cent of it. If an object could be made of close packed nuclei it would have a fantastic density, since a piece the size of a pea would weigh millions of tons. Nothing even approaching this is known on the earth, but astronomers calculate that certain stars have such a close packing of nuclei that a pea-sized portion has a mass of several tons. In contrast with this, the seven electrons of the nitrogen atom are exceedingly light, since they contribute only about 0.03 per cent to the total mass. The mass of atoms in general is essentially all in the nucleus.

Experiments also reveal that this nucleus is not one object, or even a group of similar parts. It consists, in the case of nitrogen,

of seven positively charged particles, or *protons*, and seven neutral particles, or *neutrons*. Each proton and neutron has a mass close to one avogram,² so the nucleus, and hence the atom, has a mass of essentially 14 avograms. The seven protons in the nitrogen nucleus have a charge which is equal but opposite to that on the seven electrons outside of the nucleus. The atom as a whole, then, is without charge, since electrons and protons neutralize each other.

It appears today that protons and neutrons are almost certainly not ultimate particles, but consist of smaller units. However it is not necessary, for the understanding required in elementary chemistry, that we go deeper into this very complex and uncertain field. At this writing it seems possible that there may be as many as nineteen fundamental particles.

Atomic Structure Illustrations. If one were to attempt to show the structure of a nitrogen atom with a drawing, something like that in Figure 1.1 might be used. But the feeling among scientists today is that we cannot satisfactorily show the structure of an atom with a drawing. There is too much uncertainty about the position of the electrons and the wave motion which these are believed to possess. The present trend in science is to describe these structures mathematically rather than visually.

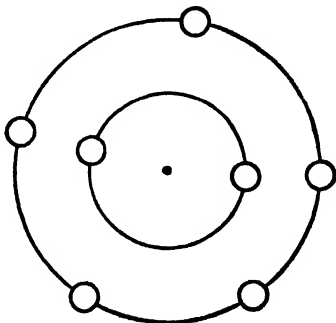


FIGURE 1.1. The Nitrogen Atom. Circles are electrons, the dot in the center is the nucleus, drawn much too large in relation to the rest of the atom

OTHER ELEMENTS

Atomic Number. When the reader understands this much about the structure of the nitrogen atom, and the nature of the subatomic particles which comprise it, he will have learned also about the composition of other kinds of atoms, because all of

² See page 15.

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them consist of a nucleus and one or more electrons. The criterion which determines most fundamentally what kind of atom one is dealing with is the number of protons in the nucleus. This is characteristic for each type and is called the *atomic number*. There are known at the present time 98 types of atoms with different proton contents, starting with hydrogen, whose nucleus contains one proton and ending with californium, whose nucleus includes 98 protons. These 98 types are the *elements* of the chemist. They are given in the table in the front of the book, together with some fundamental facts about them.

Common and Rare Elements. All material things, with the exception of radiation, electricity, and other subatomic particles, are made from one or more of these 98 elements. Most of these are quite rare, and indeed, some of them are too unstable to have been able to exist all this time on our ancient earth. They are not found in nature, but have been made in the laboratory. Francium and technetium are examples of such elements.

TABLE 1 2 Composition of the Earth's Crust *

<i>Element</i>	<i>Percentage</i>
OXYGEN	49.5
SILICON	25.7
ALUMINUM	7.5
IRON	4.7
CALCIUM	3.39
SODIUM	2.63
POTASSIUM	2.40
MAGNESIUM	1.93
HYDROGEN	0.87
TITANIUM	0.58
CHLORINE	0.19
PHOSPHORUS	0.12
MANGANESE	0.09
CARBON	0.08
SULFUR	0.06
BARIUM	0.04
CHROMIUM	0.033
NITROGEN	0.030
FLUORINE	0.027
ZIRCONIUM	0.023

Nearly all of the objects around us are made from one or more of the two or three dozen commoner elements. The twenty commonest elements in the earth's crust are shown in Table 1.2. The percentages are from a report by Anderson

THE PERIODIC LAW

Variation of Properties. The atomic numbers of the elements vary regularly from one to 98; hence it might be supposed that the properties³ of the elements vary likewise. One might imagine, for example, that the size of atoms would increase regularly going from hydrogen to californium. But at this point, if we have any misconceptions as to the complexity of nature, we lose them, because only a very few properties of atoms, such as mass and neutron content, vary at all regularly with atomic number. It is one of the annoying facts of science—annoying, that is, to those looking for simplicity and regularity—that elemental properties vary in a highly irregular manner as we go from one end of the list of elements to the other. Examination of the changes in such properties as radius and melting point (Figure 1.2) reveals many hills and valleys in the curves. However, these changes are not entirely haphazard, but rather, periodic.⁴ It is known that the number of electrons in the outer shells of neutral atoms also varies in a periodic manner with atomic number (Table 1.3); hence it is believed that most elemental properties are determined chiefly by the number of outer electrons which a neutral atom possesses.

The variation of properties with atomic number, important to chemists, is known as the *Periodic Law: Nearly all elemental properties are periodic functions of atomic number.* As a result of this periodic variation certain elements have rather similar properties. Thus, as predicted by the electron structure in Table 1.3, lithium, sodium, and potassium are similarly active⁵ metals;

³ Attributes such as density, color, hardness, and melting point.

⁴ A familiar example of a periodic variation would be shown by plotting the intensity of sound against time during the passing of a steam locomotive or the beating of a drum.

⁵ Active elements combine readily with other substances.

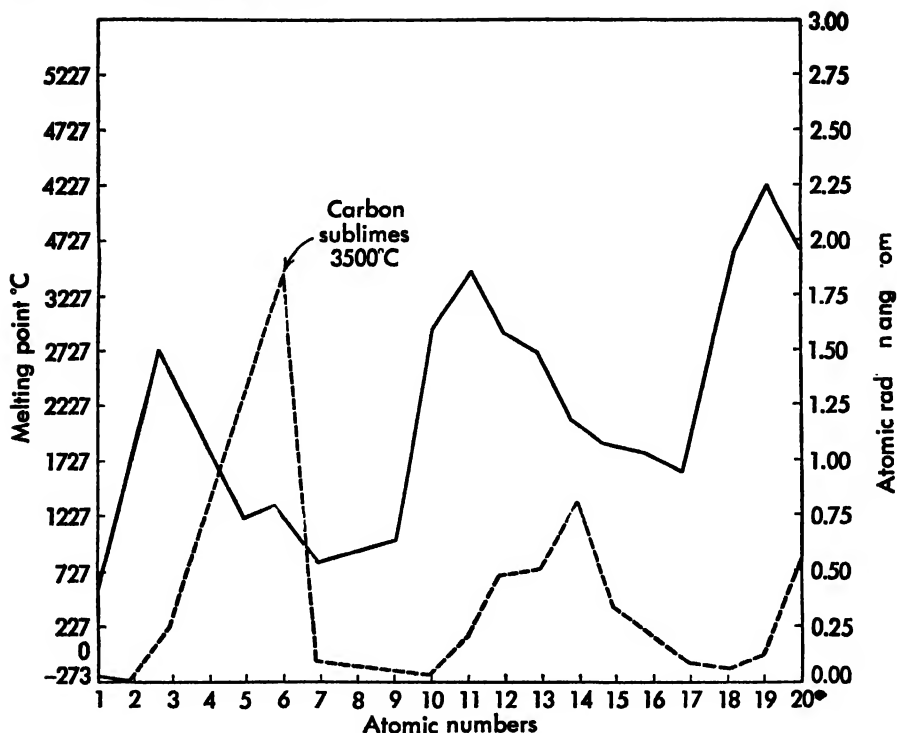


FIGURE 1.2. Periodic Changes. Variation of atomic radius (unbroken line) and melting point (broken line) with atomic number; first twenty elements.

fluorine and chlorine are highly active nonmetals;⁶ while helium, neon, and argon are very unreactive (inert) gases. With the exception of helium, the elements in each group are seen to have the same number of electrons in their outermost orbits.

Various classifications are used by chemists and others in which these elements with similar properties appear under one another. They are called periodic systems, tables, or charts. They are of value because they enable chemists to predict properties of the elements and their compounds from the positions in such tables. They are also of great help to the professional chemist in that they enable him to organize a large amount of factual information in his mind. Two systems are given at the back of the book, one based upon an early classification by the Russian chemist Mendeleeff, the other a modern system.

⁶ Metals and nonmetals are differentiated on page 41.

TABLE 1.3 Electron Structures of the First Twenty Elements

<i>Element</i>	<i>Atomic number</i>	<i>Electrons, 1st shell</i>	<i>Electrons, 2nd shell</i>	<i>Electrons, 3rd shell</i>	<i>Electrons 4th shell</i>
HYDROGEN	1	1			
HELIUM	2	2			
LITHIUM	3	2	1		
BERYLLIUM	4	2	2		
BORON	5	2	3		
CARBON	6	2	4		
NITROGEN	7	2	5		
OXYGEN	8	2	6		
FLUORINE	9	2	7		
NEON	10	2	8		
SODIUM	11	2	8	1	
MAGNESIUM	12	2	8	2	
ALUMINUM	13	2	8	3	
SILICON	14	2	8	4	
PHOSPHORUS	15	2	8	5	
SULFUR	16	2	8	6	
CHLORINE	17	2	8	7	
ARGON	18	2	8	8	
POTASSIUM	19	2	8	8	1
CALCIUM	20	2	8	8	2

Boldface numbers show electrons in outer shell

DIFFERENT FORMS OF NITROGEN

Isotopes and Ions. Returning to our nitrogen atom, it is seen to be one of the simpler types of elements, with an atomic number of seven. To be nitrogen, then, an atom must have seven protons in its nucleus. But it is important to note that *the number of both of the other types of subatomic particles present can vary.*

Under certain conditions a neutral nitrogen atom can lose electrons. There are then not enough of these to offset the seven positive charges from the protons in the nucleus. The atom is no longer neutral; it now has a positive charge. Similarly it can gain electrons under other conditions and become negatively charged because of an excess of these. When an atom or a group of atoms becomes charged, either positively or negatively, it is called an *ion*. A neutral atom which becomes an ion in this way is still regarded as the same element, however, because the proton content of the nucleus has not changed.

The neutron content of the nucleus may also vary. This is a more difficult thing to bring about, because nuclei are so small and hard to reach. However, changes in nuclei can be produced, and, indeed, are the cause of all the nuclear phenomena which are of such great interest at the present time. But even though we may not succeed in changing the neutron content of a nucleus, there are present in nature many examples of elements whose atoms contain more than one quantity of neutrons. For example, although the common form of nitrogen has seven neutrons in the nucleus, there is another form containing eight neutrons. Out of every 1000 nitrogen atoms, four will be the eight neutron kind, on the average. These have a greater mass (15 avograms) than the common form because of the extra neutron. The different types of atoms of a given element, distinguished by their neutron content and mass, are called *isotopes* of that element.

Summing up the important points covered in the last few paragraphs, it is seen that the only fixed, definite thing about the atoms of a given element is the number of protons in the nucleus. This is called the atomic number, and is constant for each element. The electron content can be varied, producing ions of the element, and the neutron content can vary, accounting for isotopes, but these are all considered as being merely different forms of the same element, as long as the proton content remains the same. The approximate masses of the most common isotopes of the elements are shown in the table at the front of the book.

MOLECULAR STRUCTURE OF NITROGEN

The discussion so far has been about the nitrogen atom. However, in spite of the enormous amount of nitrogen gas in our atmosphere, there are relatively few single nitrogen atoms therein, because the unit nitrogen particle present in the air is a *molecule* consisting of two nitrogen atoms.

Molecules. A molecule is generally a group of atoms joined together which exists as a single unit. Molecules can be likened

to chains, where the links in the chain correspond to the atoms in the molecule. The simplest chain might be thought of as one link, and in the same way the simplest molecule consists of but one atom. These are not common, however, and the great majority of molecules contain two or more atoms. For example, a molecule of water vapor is composed of three atoms, alcohol nine, those in gasoline average about 25, table sugar 45, chlorophyll (the green coloring matter in plants), 137, etc. Some molecules, such as those found in plastics, rubber, wood, and in the proteins of living cells, are giants (among molecules), since they contain many thousands of atoms each. While the analogy of the chain makes for easy visualization of molecules, the reader should bear in mind that the atoms in molecules are often joined together differently than in a row, giving various kinds of two- and three-dimensional structures.

In summary, then, while an *atom* is a particle of matter consisting of one nucleus and accompanying electrons, a *molecule* is usually a group of atoms combined with each other so as to act as a unit.

The Molecular Binding Force. The two nitrogen atoms in a molecule are bound together so tightly that it takes a very powerful force, such as the energy from a stroke of lightning, to break them apart, after which they tend quickly to combine again. An important question now arises as to the binding force which holds these atoms together so firmly.

The answer, as nearly as we can tell from the evidence, is that electrons bind the atoms together. Just how they do this, in detail, is one of the unsolved mysteries of science. There is no satisfactory way in which we can picture electrons holding atoms together, partly because no one knows the shape or shapes of an electron, and these tiny entities are variously imagined as vibrating halos (wave mechanics), spinning spheres (magnetism), and in other ways. The electron bonds which hold atoms together are also elastic, since they permit the atoms in the molecule to move toward and away from each other, in a rapid vibration. They

also permit rotation of different parts of the molecule in some cases, as if they were acting like axles.

All this gives but little help to the beginning chemistry student, and particularly to the student who does not "understand"

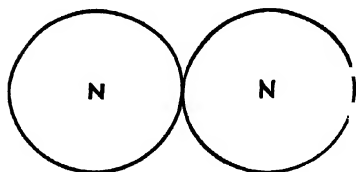


FIGURE 1.3. Simplified Drawing of a Nitrogen Molecule.

unless he can form a mental picture. But the plain truth is that scientists themselves have no adequate mental picture to pass on to the student of how electrons hold atoms together. Their conclusions are based upon experimental data and mathematical computations

which do not yet permit the satisfactory description of how a magnified electron bond would appear if it could be seen.

A simple but not completely suitable way in which binding electrons can be pictured is that they make a path (molecular orbital) around the atoms in a molecule and hold the latter together in a manner which can be compared crudely to the way in which sheep dogs might keep two sheep together by running rapidly around them. If we picture this electron path as being that of a figure eight on its side, then the nitrogen molecule can be illustrated by the drawing in Figure 1.3. Actually such molecular orbitals are three dimensional, rather than in two dimensions as shown here.

In this drawing each letter N means a nitrogen atom complete except for the electrons which it has furnished for bonding, and the latter are assumed to be in the figure eight path. Drawings of this sort are useful in helping to explain some fundamental properties of molecules, and they will be employed occasionally in the next few pages. The reader should remember, however, that they are included as visual aids to learning rather than as true pictures, because certain fundamental objections arise if one intends such drawings to represent the actual structure of a molecule.

When the reader understands this much about how two atoms of nitrogen are held together, he will have learned something more general than merely some of the chemistry of nitrogen,

because the atoms in most molecules are bound in a similar way. Only certain substances such as table salt (page 128) have their atoms held together in a different manner which will be described later.

Shared Electrons; Covalence. The electrons which hold atoms together as described above are said to be *shared* by the two atoms, and the molecules so formed are called *covalent* molecules. These terms, used often in chemistry, should become familiar to the reader.

The number of electrons which an atom gives for sharing purposes is called its *covalence*. In a nitrogen molecule each nitrogen atom is thought to share three of its outer electrons, in which case there are six electrons in the figure eight orbit, three from each atom. This makes the covalence of nitrogen three.⁷ Common valences for the important elements are shown in the table at the front of the book.

Rule of Eight. A question now arises: When an atom becomes part of a molecule, how many electrons does it share in forming the bond and how many remain unshared? In many instances it appears that the number of shared electrons, *plus* the number remaining in each atom's outer shell, equals eight. For example, if nitrogen atoms each furnish three electrons for sharing in the formation of nitrogen molecules, then the total number shared will be six, and the number remaining in *each* atom's outer shell (unshared) will be two, giving a total of eight. The tendency of electrons to rearrange in this way in molecules is sometimes called the rule of eight.⁸ It seems to hold true in many molecules, but

⁷ However, covalence is only one kind of *valence* (the number which shows the combining capacity of an atom or an ion). Electrovalence will be described later.

⁸ There is no connection between the rule of eight and figure eight electron paths. When two similar atoms combine to form a covalent molecule, the equation $n + s = 8$ can be used to find the number of electrons (s) which each atom furnishes for sharing according to the rule of eight. n is the original number of electrons in each atom's outer shell.

The rule of eight follows from the Lewis-Langmuir octet theory, developed during the period 1916-19. Since that time atomic structure theory has been changed and improved, notably by the introduction of wave mechanics. Theory based on the latter is, however, too complex to include in an elementary text.

there are exceptions, notably in the case of the light atoms, like hydrogen, where the number is less than eight.

The Dot Convention. There is a convention in general use in chemistry for showing the number of electrons binding atoms together and the number remaining in each atom's outer shell. In this convention dots are used for electrons, together with a letter or letters designating the remaining part of each atom. Thus the nitrogen molecule is written :N::N: , each N signifying an atom of nitrogen minus the outer shell of electrons. The ten electrons from the two outer shells are then designated by ten dots. Those *between* the letters are shared, or figure eight, electrons. The remainder—two for each atom—are unshared. This furnishes a quick, satisfactory method of showing electron configuration as long as the reader remembers that the electrons are probably not stationary and are not necessarily in a two-dimensional plane. In this representation the electrons in the underlying shells are included as part of the letter N.

Symbols and Formulas. The chemist has still another, simpler way of showing the composition of a nitrogen molecule which omits the electron dots. He writes N_2 . The letter N now means a whole atom of nitrogen, i.e., a nucleus plus seven electrons (contrast with the meaning in the last paragraph and in the figure eight drawings). The abbreviation "N" used in this way is called the *symbol* of nitrogen. The symbols of all the elements are shown in the table in the front of the book.

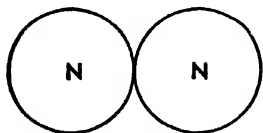


FIGURE 1.4

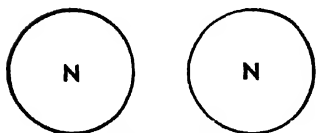


FIGURE 1.5.

The subscript 2 after the nitrogen shows that there are two atoms of nitrogen in a molecule. Note the difference between N_2 , 2N and 2N_2 . N_2 means a molecule of nitrogen (Figure 1.4) while 2N means two separated atoms of nitrogen (Figure 1.5).

2N_2 means two separated molecules of nitrogen (Figure 1.6).

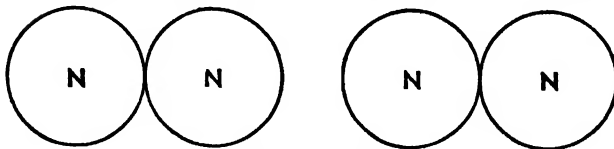


FIGURE 1.6.

Groups of symbols ^{or} written together to show the composition of a molecule are called *formulas*. These do not give information about electron distribution but tell the number and kinds of atoms in the molecule. The formula N_2 is exceedingly simple, as formulas go. In contrast with this, for example, consider one of our most complicated formulas, that of hemoglobin, the colored substance in red blood corpuscles. It is believed to be:



This molecule therefore consists of 2952 carbon atoms, 4664 hydrogen atoms, 832 oxygen atoms, 812 nitrogen atoms, 8 sulfur atoms and 4 atoms of iron.

Besides telling what atoms or molecules are being described, symbols and formulas have a quantitative significance, e.g., N_2 refers to 28.016 avograms of nitrogen, CO_2 means 44.01 avograms of this gas, containing 12.01 avograms of carbon and 32.00 avograms of oxygen. Symbols and formulas are also used upon occasion to mean a much larger weight of matter than can conveniently be expressed with avograms—in fact, *any* amount whose mass is *numerically* the same as that of single (average) atoms or molecules but is expressed with different units. Thus, N_2 can also mean 28.016 grams, or pounds, or tons of nitrogen if a calculation is required with these units.

ATOMIC AND MOLECULAR STRUCTURE OF OTHER AIR MOLECULES

If the reader is having his first contact with chemistry, he is perhaps rather saturated with new terms and ideas at this point. Without going further in theory or terminology, therefore, let us

drill in the use of these newly learned concepts by applying them to the other components of the air shown in Table 1.1.

Oxygen. Oxygen is the second most abundant air molecule. The oxygen atom is not greatly different in structure from that of nitrogen. Its nucleus, for the common form, consists of 8 protons and 8 neutrons; this gives oxygen an atomic number of 8 and a mass of 16 avograms. Traces of two other isotopes exist, containing 9 and 10 neutrons in the nucleus. The positive nuclear charge is neutralized by 8 electrons outside of the nucleus. These are in two shells, the inner one containing two electrons and the outer one six.

The oxygen molecule, like that of nitrogen, consists of two atoms. The rule of eight postulates the sharing of four electrons, leading to the structure $::O::O::$, and while some authorities believe such a structure exists under some conditions, there is in general the feeling that, at low temperatures at least, a more complicated structure must be present to account for the fact that liquid oxygen is attracted to a magnet. The symbol for oxygen is O and the formula for the molecule is O_2 .

Argon. Argon is the third most abundant element in dry air. Most of its atoms have nuclei which consist of 18 protons and 22 neutrons; hence the argon atom weighs 40 avograms in the common form, but two other isotopes also exist (36, 38 avograms). The argon nucleus has two electrons close to it, eight more farther out, and another eight in the outermost shell. Each atom of this element hence contains the proper number of electrons in its outer shell to satisfy the rule of eight. Sharing electrons with other atoms is consequently not necessary to produce this stable number; we thus account for the fact that argon is an unreactive substance which exists in the air in molecules consisting of only one atom. The gases: helium, neon, krypton and xenon (present in traces in the atmosphere) also exist as monatomic molecules, and each of their atoms (except helium) contains 8 electrons in the outermost shell. The group is called the *inert gases* because of the general lack of chemical activity.

Hydrogen. Let us consider the substance hydrogen next, before water, since it is a constituent of the latter. Hydrogen exists only in traces in the air at the earth's surface, but at high altitudes it probably makes up a greater percentage, because its lightness and high molecular speed permit it to move greater distances against gravity than other gas molecules.

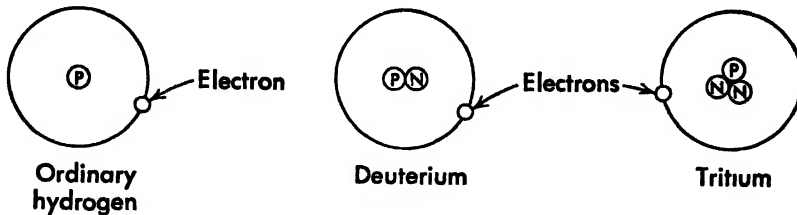


FIGURE 1 7 Structures of Hydrogen Isotopes.

Ordinary hydrogen atoms consist of only one proton and one electron, making this element the lightest and the simplest in structure of the entire 98. Two other isotopes are known containing one and two neutrons in addition. These three forms of hydrogen are shown in Figure 1.7. The two less common isotopes have received the special names of deuterium and tritium, contrary to the general rule that isotopes of the elements be distinguished by mass (as uranium 235) rather than by special names. At ordinary temperatures hydrogen exists as diatomic (two atom) molecules, H_2 , in which both electrons are shared (H:H).

Water Vapor. Water vapor and carbon dioxide are the two remaining substances shown in Table 1.1. These are fundamentally different from the other molecules in the atmosphere which have just been described in that their molecules contain more than one kind of element. Substances of this type are called *compounds*. Let us consider water vapor first.

Water vapor molecules are made up of two hydrogen atoms and one oxygen atom, giving the familiar formula H_2O . The three atoms form a V-shaped molecule as shown below. This



shape is of great importance in that it influences many of the properties of water (page 115).

A significant characteristic of compounds is their constancy of composition. Water molecules, for example, contain two

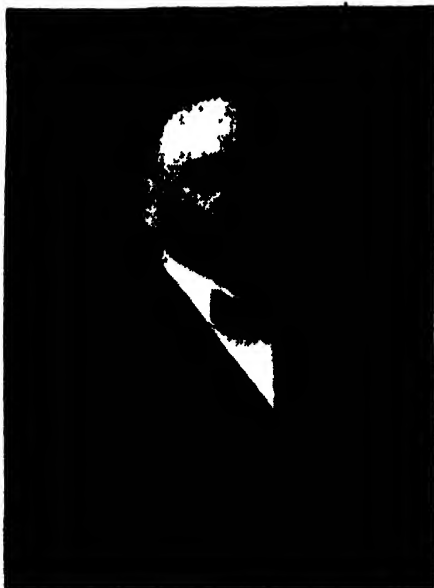


FIGURE 1.8. E. W. Morley (1838–1923). Professor of chemistry, Western Reserve University. Known for his highly accurate experimental work on the percentage composition of water.

hydrogen atoms having an average mass (considering isotopes) of 1.008 avograms each and an oxygen atom with a mass of 16.000 avograms on the average. This is assuming the virtually fixed ratio of isotopes which is usually found in nature. The weight percentage of hydrogen in the average water molecule is then given by the expression:

$$\frac{(2.016)}{(18.016)} = 0.1119$$

$$= 11.19\% \text{ hydrogen}$$

The remainder, 88.81 per cent, will be oxygen. Since vast numbers of water molecules are required for a chemical analysis, it will be these average results which will be obtained, rather than the different values

for the composition of the individual water molecules containing specific isotopes of hydrogen and oxygen.

The constancy of composition of pure compounds was shown to be true by analyses carried out many years ago. Known as the *law of definite composition*, it was one of the early foundation stones upon which the science of chemistry was built: *All samples of a given pure compound will have the same percentage by weight of its constituent elements.* This is one of the fundamental ways in which we distinguish between a compound and a mixture, since obviously the composition of the latter can be varied at will.

Carbon Dioxide. The final substance in Table 1.1 is the compound carbon dioxide. Its molecule consists of two atoms of oxygen joined to one atom of carbon by shared electrons. Carbon atoms have but four electrons in their outer shell, as shown in Table 1.3; accordingly, they must give all of these for sharing, and share four more, in order to conform with the rule of eight in this compound, at least in the symmetrical form of the molecule $::O::C::O::$.

CLASSIFICATION OF MATTER

Mixtures and Pure Substances. This concludes the first attack upon the chemistry of the air. From the discussion so far it is evident that matter exists as two varieties: *mixtures*, composed of two or more different kinds of molecules which are not in a fixed ratio, such as air, granite, or a sugar solution in water; and *pure substances*, containing only one kind of molecule. Pure substances in turn are either *elements*, whose molecules consist of atoms all of which have the same atomic number, or *compounds*, whose molecules consist of atoms having two or more atomic numbers, i.e., consist of two or more elements.

Finally elements themselves fall roughly into two groups, the *metals* and the *nonmetals*, with a few elements occupying intermediate positions between the two. Metals are substances having a characteristic luster. They are malleable (can be hammered into thin sheets), ductile (can be drawn into wires), and in general are good conductors of heat and electricity. Iron, sodium, and copper are examples of metals. Nonmetals are not as similar to each other as metals, but in general they are without the luster, malleability and ductility which characterizes the latter. They also conduct heat and electricity more poorly than metals.

TABLE 1.4 Classification of Matter

MATTER	{ Mixtures (different molecules not in a fixed ratio)	
	{ Pure substances (one kind of molecule)	{ Compounds (H_2O , CO_2)
		Elements { Metals (Fe, Na, Cu) Nonmetals (S, N, C)

Sulfur, nitrogen, and carbon are examples of nonmetals. A classification of matter according to the outline just presented is given in Table 1.4.

Experimental Determination of Types of Matter. The reader can now distinguish *theoretically* between mixtures and pure substances, elements and compounds. But chemistry is an *experimental* science, and this fact can perhaps best be emphasized here by describing briefly a very few of the methods for distinguishing between various types of matter.

Many mixtures can be identified as such by their appearance, as for example a piece of granite. In more finely divided mixtures, where the heterogeneous nature is not apparent to the eye, it is possible to take advantage of differences in behaviour of the components. A mixture of sand and sugar, for example, can be shown to be a mixture by dissolving the sugar in water. A mixture of small particles of iron and copper can be separated with a magnet. A solution of salt in water, which looks like a pure substance, can be shown to contain at least two components by tasting it, or by boiling off the water, whereupon the salt residue will be apparent. Not all mixtures are this easily separated. Chemists do not yet know all of the components in the natural mixtures we call petroleum, for example.

Samples of pure substances, on the other hand, behave the same throughout, and no separation into components takes place when such operations as boiling, filtering, or centrifuging are carried out. Pure substances, furthermore, have constant boiling points (if they are liquids) and constant, sharp melting points (if they are solids). These criteria all assume that no chemical changes take place during the testing, of course. If chemical changes do take place, as when running a melting point, for example, the pure substance automatically becomes a mixture, and behaves like one.

Previously discovered elements and compounds are identified today and therefore distinguished from each other by their characteristic properties. A yellow crystalline solid which melts

at $112.8^{\circ}\text{C}.$, is soluble in carbon disulfide, and burns with a blue flame to form a colorless gas with a choking odor, is almost certainly sulfur. As further identification, a piece of burnished copper put into the cold carbon disulfide solution of the substance will turn black due to the formation of a film of copper sulfide. A colorless liquid with a rather characteristic odor, which boils at $80.1^{\circ}\text{C}.$ and has a refractive index⁹ of 1.5011 at $20^{\circ}\text{C}.$, is the substance benzene.

In the early days of chemistry, when very few properties of matter were known, such identifications were much more difficult. Elements were materials which could not be decomposed further, and lists of those times often contained substances like silicon dioxide, which chemists could not then break down, but which we now know are compounds rather than elements. However, with such advances as the setting up of the periodic system and the work of Moseley, who showed that atomic numbers could be determined from X-ray data, it became clear which substances were elements and which were compounds.

Analytical chemistry is the branch of the science which deals with the identification and composition of matter.

Self Study Questions

1. What are the five chief types of molecules in humid air in the order of decreasing abundance?
2. Define electron, proton, neutron, nucleus, isotope, ion.
3. Describe the atomic structure of a nitrogen atom. How is that of an oxygen atom different? Of a hydrogen atom?
4. What is the approximate mass, in avograms, of a proton, a neutron, and an electron?
5. One isotope of the element tin has 65 neutrons in the nucleus. What is the approximate mass of such a tin atom?

Answer: 115 avograms.

6. Chlorine atoms have seven electrons in their outermost shell. Using the dot convention and the rule of eight, show how two

⁹ $\frac{\text{Speed of light in a vacuum}}{\text{Speed of light in benzene}} = 1.5011$

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chlorine atoms are held together in a covalent molecule. (Footnote, page 35.)

7. What must be the covalence of chlorine from the answer to (6)?
8. From the covalence of chlorine, show the structure of carbon tetrachloride, CCl_4 , using the dot convention and the rule of eight.
9. Explain in terms of the rule of eight why an argon molecule contains but one atom.
10. State the law of definite composition. Calculate the percentage of oxygen in carbon dioxide.
11. Distinguish between a compound and an element. Give examples of each. Distinguish between an atom and a molecule.
12. Use the dot convention to show the structure of water and carbon dioxide molecules.
13. Classify the different varieties of matter. Give examples of each kind.
14. The letter "N" has been used in three different ways in this chapter, i.e., meaning three different portions of a nitrogen atom. Can you describe them?

II

Molecular Motion and Its Consequences

If a miraculous being the size of a molecule could exist, and he could examine the air in a quiet room, the view he would get would be startling. Such a being would of course need a far different kind of light than we use, and a fantastically greater quickness of vision than that of a normal person before he could see anything at all. Assuming our imaginary being to be so constructed, his concept of the air would be totally different from ours.

He would observe that air consisted of the tiny particles discussed earlier—the molecules. But it would also be apparent to him that each molecule was surrounded by a considerable region of space, since only one volume in several thousand volumes of air is actually molecules. He would observe these molecules to be in a violent state of activity. They would be flying around in all directions at high speeds, colliding with each other and with the walls, ceiling, and floor of the room. During these collisions they would exhibit perfect elasticity on the average (assuming no radiation loss). By that is meant that two molecules, colliding head-on at the same speeds, would rebound and move in opposite directions without loss of velocity.

The appearance of a tiny portion of the atmosphere to a molecular sized being might be likened crudely to an unusual basketball game in which several hundred basketballs are being thrown around at the same time, but for several reasons this is not a satisfactory analogy. Basketballs do not collide with perfect elasticity, nor do they move nearly fast enough to compare with

molecules. They also do not visibly exhibit motions similar to those of electrons in the atoms or atoms in the molecules.

This violent molecular motion would be present in the air of a perfectly quiet room; it would not be due to air currents or wind, because the mass motion which we know as the wind is superimposed and different from the other. This point can be made clearer by using as an analogy a popcorn cart with the cooker going and popcorn flying around in it. At the same time the cart might be pushed down the street, causing all of the flying pieces of corn to move with it. This latter motion would be similar to the wind.

Molecular Motion a General Phenomenon. Molecular motion is not only characteristic of the air. All gases behave similarly, and to a lesser extent all liquids. The molecules in solids are also active, but here the motion is confined to a region around one spot in the solid which is allotted to each molecule. Molecular motion in solids is therefore *vibrational* (in one place) rather than *translational* (from place to place). The world of molecules is one of ceaseless activity.

Many years ago it was suggested that gas molecules must have perfect elasticity, and be relatively far apart and in rapid motion to account for their known behaviour. This pictured state and its mathematical consequences was called the *kinetic molecular theory*, and it was advanced to explain the compressibility of gases, the spreading of odors, the increase of pressure with temperature at constant volume, and, indeed, the phenomenon of gas pressure itself. Today this molecular picture has been shown to be true in so many ways that it is accepted as fact rather than as theory.

Brownian Movement. For example, if matter in a very fine state of subdivision, such as a smoke particle suspended in the air, be examined with high magnification, the effect of this molecular motion can be clearly seen, even though the molecules cannot. The smoke particle is seen to jump around irregularly and spin in various ways, as if continually being run into with

invisible objects. This is because these molecular collisions take place unevenly. It has been calculated that about ten quadrillion (10^{16}) molecules will run into such a particle every second, and it follows statistically that in the case of such a large number of collisions an excess of several hundred on one side or another is quite probable at any given instant, thus accounting for the irregular motion of the particle.

This movement of small particles of matter produced by molecular collisions is called the *Brownian Movement*, after the English botanist Brown who observed it in a suspension of pollen grains in 1827. It is probably the most direct evidence we have for molecular motion; taken together with a great accumulation of other evidence, it leaves no doubt in the minds of present-day scientists as to the reality of such motion.

Gas Pressure. When air molecules strike the walls of a room, or other container, they cause the phenomenon of *gas pressure*. This is familiar to all in the case of compressed gases, as in automobile tires or air lines. But the pressure of the air also exists all over the surface of the earth as the result of collisions between air molecules and surface objects. Each colliding molecule contributes only a tiny bit to this pressure, but the number of collisions per second is so enormous (10^{16} for a smoke particle) that a considerable total pressure of some 14.5 pounds per square inch results, or in scientific units, about 1000 grams per square centimeter. This pressure is not noticed as one goes about one's daily tasks because it is offset by a similar internal pressure. It does become apparent, however, when external pressure is changed rapidly, as in a descending elevator or when going down a steep hill in a car.

Kinetic Energy. An important fundamental fact about gases is that under similar conditions (volume, temperature, number of molecules), all gases exert the same pressure, regardless of the mass of their molecules.¹ Thus, 10^{21} oxygen molecules in a

¹ From Avogadro's Law: Equal volumes of all gases at the same temperature and pressure contain the same number of molecules

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container at 25°C . will exert the same pressure as 10^{24} hydrogen molecules in a similar container at the same temperature, in spite of the fact that each individual oxygen molecule has some 16 times the mass of each hydrogen molecule, and exerts a greater striking power in a single collision with the walls of the container. The hydrogen molecules overcome this handicap by moving faster, and therefore by colliding with the walls more frequently. Gas pressure is determined, not by a single molecular collision, but by the number of collisions per second. In the example just given the hydrogen molecules collide with the walls of the container enough oftener per second to make the measured hydrogen gas pressure equal to that of the oxygen gas.

The pressure which a gas exerts is proportional to the average *kinetic energy* of its molecules, which is a quantity equal to one half the molecular mass times the square of the average velocity, or $\frac{1}{2}mv^2$. At any given temperature all gases have the same average kinetic energy, and if their molecular mass is large, their velocity will be proportionally small.

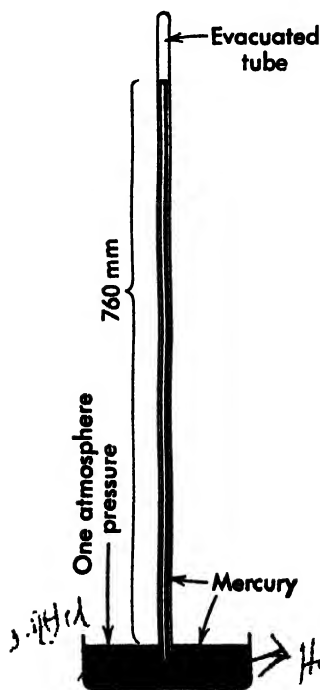


FIGURE 2.1. A Mercury Barometer.

the (evacuated) tube, since there is virtually no gas pressure at the other mercury surface to oppose the rise. At sea level the atmospheric pressure often elevates such a column about 760 mm. The amount of pressure to cause just this rise is therefore called *one atmosphere*. Pressure is most commonly measured, however,

The Barometer. There are several ways of measuring pressure. The scientist usually employs a mercury barometer. This is a glass tube, open at the bottom and closed at the top, containing a column of mercury (Figure 2.1). The pressure of the atmosphere or other gas on the mercury at the lower, open end causes this liquid to rise in the

not in atmospheres, but by the difference in heights of the two mercury surfaces. This is a linear measurement; hence, we have values for pressures such as 743 mm., 83.4 cm., 28.74 inches, etc.

Besides its use in determining atmospheric pressures, the barometer is employed as a general instrument for gases, covering a wide range of pressures. The reader is probably also familiar with the aneroid type of barometer, in which the indicator is operated by the swelling or contraction of a gas-filled container caused by changes in atmospheric pressure.

Pressure and Altitude. As the result of their rapid motion, and the very slight gravitational pull upon their tiny masses, air molecules are not held tightly to the earth's surface, but fly around in a zone many miles thick which constitutes our atmosphere. We are not sure to what height this zone extends, but triangulation measurements upon the northern lights (an air phenomenon) place its top as far as these are concerned at about 600 miles.

Air molecules are under a constant force pulling them in one direction (gravity) and another force, caused by molecular collisions, tending to scatter them in all directions. These two forces acting at the same time produce a vertical concentration gradient which causes a gradual thinning out or rarefaction as the distance from the earth increases. One might liken it to many women at a bargain counter, where the force acting in one direction (the bargains) and the force acting in all directions (random jostlings) tend to produce a concentration gradient perpendicular to the bargain counter, with the highest concentration right at the counter.

The concentration gradient in the atmosphere produces the familiar phenomenon of reduced pressure at high altitudes. If temperature corrections can be made, altitude can be calculated rather accurately from pressures, but this is difficult to do in some conditions of weather. The drop in air pressure (and concentration) at high altitudes may be so pronounced that the breathing rate must be considerably increased, and this is one

of the reasons why high altitude climbing is physically tiring;
the climber has difficulty taking in enough oxygen.



FIGURE 2.2. (a) Robert Boyle, English natural philosopher (1627-91) (b) John Dalton, English chemist and physicist (1766-1844). Laws named after these men and based upon their work are described in this chapter. From Black and Conant, *New Practical Chemistry*, Revised Edition. Copyright, by The Macmillan Company.

Partial Pressures. The pressure exerted by a mixture of gases is made up of a number of *partial pressures*, one for each type of molecule present. The sum of these will equal the total pressure. Each of the partial pressures, in turn, is proportional to the number (and concentration) of molecules of that particular species in the sample of mixed gases. Thus if a mixture of 10^{12} oxygen molecules and 10^{12} nitrogen molecules exerts a total pressure of 800 mm. on the container, then each gas will have a partial pressure of 400 mm. If a mixture of 0.5×10^{12} oxygen molecules and 1.5×10^{12} nitrogen molecules exerts a total pressure of 800 mm., then the partial pressure of the oxygen will be but 200 mm., and that of the nitrogen will be 600 mm.,

because for each oxygen molecule there are three nitrogen molecules.

In the same way, nearly four fifths of the pressure exerted by the air is due to nitrogen molecules, and about one fifth is due to oxygen molecules. These partial pressures can be calculated from the data in Table 1.1, by multiplying 760 by the fraction of each gas present (as 3/10,000 for carbon dioxide, etc.). For average air we get the values shown in Table 2.1.

TABLE 2.1 Partial Pressures of Air Components

<i>Air component</i>	<i>Partial pressure</i>
NITROGEN	587.1 mm
OXYGEN	157.9
ARGON	7.1
WATER VAPOR	7.6 (approximate)
CARBON DIOXIDE	0.2 (approximate)
HYDROGEN, NEON	
HELIUM, KRYPTON, XENON	0.1 (approximate)
<i>Total pressure</i>	<i>760.0 mm</i>

The points just discussed are known in summarized form as *Dalton's Law of Partial Pressures*: *The total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the components.* It is useful in enabling one to predict how the pressure will change if the amount of one of the gas components is varied at constant volume and temperature. Thus, if a sample of the average air above were thoroughly dried without changing its volume or temperature, its total pressure would become 752.4 mm. (Why?)

RELATION BETWEEN VOLUME AND PRESSURE

If the volume of a gas be diminished by compressing it, then the concentration of gas molecules (number per unit volume) in the final volume will be greater than the original concentration, and the number of collisions with the walls per second will be greater, meaning the pressure will be greater. It can be shown both theoretically and experimentally that, for a given specimen

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of gas at constant temperature, volume and pressure are inversely proportional, or:

$$\frac{\text{Starting volume}}{\text{Final volume}} = \frac{\text{Final pressure}}{\text{Starting pressure}}$$

This relationship is known as *Boyle's Law*: *At constant temperature the volume of a given specimen of gas will vary inversely with its pressure.* Mathematically, this becomes:

$$\frac{V_s}{V_f} = \frac{P_f}{P_s} \quad \text{or} \quad \frac{V_1}{V_2} = \frac{P_2}{P_1}$$

Thus, according to Boyle's Law, if a sample of air has a volume of 268 ml. at 765 mm. pressure, its volume will become 2680 ml. at 76.5 mm. pressure, and 1.34 ml. at 153,000 mm. pressure. Gas problems involving Boyle's Law are given in Chapter XXVI.

EFFECT OF TEMPERATURE UPON MOLECULAR ACTIVITY

The effect of temperature upon a gas is more complicated. To begin with, by temperature we mean a degree of hotness or coldness brought about by a certain state of translational molecular activity. If molecules move more rapidly than usual we say they are hot, and if they move more slowly they are cool. Water molecules in polar air have a lower average velocity than those in tropical air; these in turn move less rapidly than the water molecules which make up steam.

Molecular Motion. Let us elaborate this point by considering

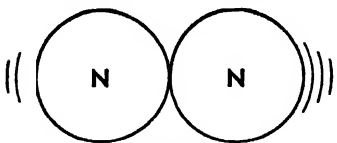


FIGURE 2.3.

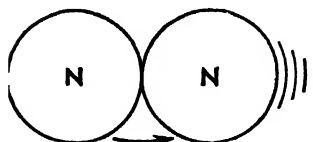


FIGURE 2.4.

the nitrogen molecule described earlier. This molecule will have certain motions associated with it which can be shown with figure eight diagrams. First, the nitrogen atoms making up the molecule will be moving toward and away from each other in vibrational motion (Figure 2.3). The whole molecule will spin in space in various ways (rotational motion, Figure 2.4).

The whole molecule will move through space (translational motion).

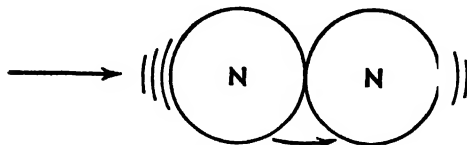


FIGURE 2.5.

As the temperature of a gas increases, all of these movements associated with its molecules become more rapid, on the average. The electrons are thought to assume positions farther from the nuclei, the molecule vibrates, spins, and moves through space faster as it becomes hotter. A hot and a cold nitrogen molecule can then be contrasted by use of the following drawings:

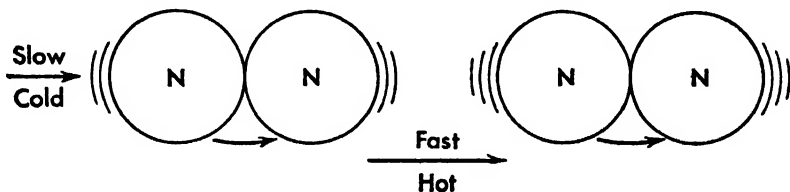
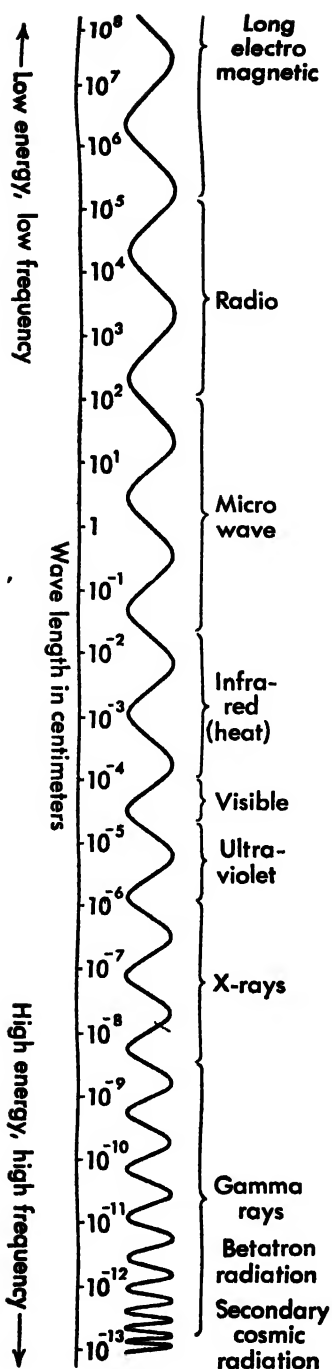


FIGURE 2.6.

Heat, then, is transmitted from molecule to molecule as the result of molecular collisions. Thus, an aluminum saucepan of water heated with a gas burner is thought to go through the following process. Rapidly moving (hot) molecules from the burning gas hit the underside of the pan causing aluminum atoms therein to vibrate more rapidly. This increased vibration is efficiently and rapidly passed through the pan (because aluminum is a good heat conductor) so that very quickly thereafter the aluminum atoms on the inside of the pan also become hot. Water molecules striking these rapidly vibrating aluminum atoms have their vibrational, rotational, and translational movements increased, which means the water becomes hot.

But this is not the whole story about temperature. The subject of radiation must be touched upon, although this is usually covered in the science of physics.



Radiation. *It is a fundamental property of matter under certain conditions to give off, as radiation, a portion of its mass, usually a very small portion, whereupon the specimen of matter becomes less energetic, i.e., its electronic, atomic and molecular movements tend to become less active. Matter can also absorb radiation, in which case these movements become more active. Radiation can be emitted or absorbed by any type of matter having oppositely charged parts which move with respect to each other, such as an atom whose electrons move in relation to the nucleus, or a polar molecule whose differently charged parts spin or vibrate. While both positively and negatively charged parts are required, we tend to think of the emission or absorption of radiation as having chiefly to do with electrons.*

The radiation emitted in this manner then takes on a group of properties so unusual that the human mind has difficulty in comprehending them. These include values for velocity up to 186,000 miles per second; a mass equivalency² of one milligram for some three million cubic miles, in the case of the sun's radiation; and wave constants, i.e., waves from thousands of

² The calculated mass lost by the matter which gave off the radiation.

FIGURE 2.7. Span of Radiation, or Electromagnetic Spectrum. Note how small a portion the human eye can detect.

miles to sextillionths of an inch in length, and having frequencies from under a hundred to sextillions per second. Radiation is also discontinuous, being made up of tiny units known as photons.

One of the chief fundamental problems in natural science is that concerned with the nature of radiation and the mechanism of its formation and absorption. It should be pointed out, however, that the unusual properties of radiation do not appear abruptly with the formation of that material. As matter is subdivided into units of smaller and smaller mass there appears to be a continual increase in (a) the velocity of these units and (b) their wave properties, and while these two reach maximum values in radiation, they are associated to a lesser degree with matter itself.

Radiation and Temperature. The electrons of substances giving off radiation become less active, and this in turn produces a slowing down of other types of motion, and consequently a drop in temperature. When this happens a substance is said to radiate away its heat.

On the other hand radiation can be picked up as well as lost. The electrons which absorb it become more energetic, causing atomic and molecular motions to increase, and a rise in temperature results. In general, radiation tends to be picked up by electrons which vibrate, or tend to vibrate, similarly to the electrons which originally gave off the radiation. Thus, radiation from the oscillating electrons in a broadcasting antenna tends to be picked up by those in a receiving antenna, making possible such things as radio and television. The radiation comprising the yellow light given off by the electrons of hot sodium atoms tends to be absorbed by those in cooler sodium atoms. The radiation given off by electrons holding atoms together in a hot molecule is thought to be picked up by electrons binding colder atoms together in other molecules, making these more active, and therefore causing a rise in temperature.

Radiation is thus seen to be a space-spanning method whereby

active molecules can give part of their energy to less active molecules at a distance. The sun is, of course, our prime source of this form of energy, since it continually makes up for the radiation which the earth's electrons are losing, by pouring in a new supply. In the absence of the sun, at night, heat rather quickly leaves the earth's surface and the objects on it; everyone is familiar with this process and the corresponding drop in temperature. But before any extreme cooling takes place the sun rises and things once more warm up.

It should be noted that an object does not have to be hot to lose radiation; it can do so at ordinary temperatures. We now have sensitive film which can photograph a person in darkness. The radiation which he gives off acts upon the photographic emulsion. Even very cold objects emit a feeble radiation, but if they are large enough this can be detected. The planet Saturn, for example, gives off a measurable radiation (in addition to reflected sunlight), although its temperature is probably below 100°K . As the temperature of an object drops the radiation it emits becomes less energetic and of longer average wave length.

The purpose of including this brief discussion of radiation has been to make it clear that molecules become hotter, and therefore more active, not only by collisions with hot molecules, but also by absorption of radiation from hot molecules at a distance, sometimes at a vast distance. Likewise they slow up and become cooler, not only by collisions with colder molecules, but also by loss of radiation.³ Infrared radiation appears to be most effective in causing temperature changes.

Relation between Gas Temperature and Volume. When a sample of air or other gas is heated in an expandable container, such as a thin rubber balloon, the gas volume increases and

³ However, the chief air molecules (oxygen, nitrogen, argon) do not absorb heat radiation in significant amounts because of the symmetry of their structures. A molecule must be "polar," i.e., must have the center of its positive charge at a different point in space from the center of its negative charge, before it can absorb radiation from rotating or vibrating molecules. This explains why the air is not heated to an appreciable degree by the sun's radiation, but must get its heat by molecular collisions with the warm earth.

enlarges the container. This is because the hot gas molecules move faster, causing them to strike the container harder and more often. The expansion is then the result of the increased pressure. Various phenomena in nature are in part due to the expansion of heated air, such as the formation of "thunderhead" clouds in summer, and seacoast breezes which tend to blow in the same direction at the same time of day. However, the rising of hot air which is involved in these weather conditions is also in part due to convection caused by density differences. The first thermometer (Galileo) used the expansion of air to measure rise in temperature.

If pressure be kept constant, the expansion of a sample of air or other gas which accompanies heating is determined by the change in absolute temperature (page 16). This volume-temperature relationship, found by experiment many years ago, is known as *Charles' Law*: *At constant pressure the volume of a given specimen of gas varies directly as its absolute temperature.*

$$\frac{\text{Starting gas volume}}{\text{Final gas volume}} = \frac{\text{Starting absolute temperature}}{\text{Final absolute temperature}}$$

or $V/V_f = T/T_f$, or simply $V_1/V_2 = T_1/T_2$. Absolute temperatures must be used in these calculations. Thus, if 200 ml. of a gas is at 27°C. (300°K.), its volume will become 400 ml. at 327°C. (600°K.). The volume of a gas may vary enormously with the temperature, because of the tremendous possible range of the latter. Hence, the sample of gas just mentioned would be expected to have a volume of some 2×10^7 ml. at 30 million degrees, which may be the temperature in the interior of the sun, while at -261°C. (12°K.) it would occupy only 8 ml., and at -273°C. (Absolute zero) its volume would be nothing at all, according to Charles' Law.

Failure of Charles' Law at Low Temperatures. This last statement is not in accordance with the experimental evidence, and Charles' Law is obviously at fault in the region of absolute zero, since matter does not disappear as the result of extreme

cooling. Actually as we lower temperature the gas eventually becomes a liquid, then a solid, with an essentially constant

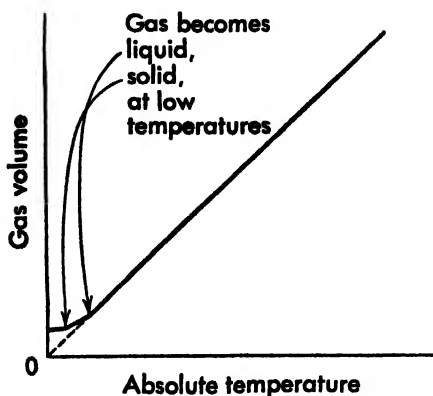


FIGURE 2.8. Variation of Gas Volume with Absolute Temperature. The straight line, dotted near the origin, shows the relationship according to Charles' Law. The bent portion shows how the experimentally determined volumes differ from those predicted by Charles' Law at low temperatures.

used a tire pump. This is in part because of the work done, i.e., gas molecules ^{moving at} bouncing off the ^{compression} piston are speeded up, for the same reason that a baseball leaves the bat of the home run hitter faster than it is thrown by the pitcher. The attractive forces between molecules also become more important at high pressures, and this may bring about a rise in temperature, as explained in the following paragraph.

When a molecule approaches another molecule, both are believed to speed up just before a collision, because of the attractive force between them. Immediately before and after the collision the kinetic energy is therefore high. As the molecules recede after the collision they are thought to slow up, much as a bouncing golf ball slows up as it leaves the earth. However, the golf ball does not permanently leave the earth. Presently it is drawn down again, and eventually the two cling together. Gas

volume from that point on. The general behaviour of gases is indicated by the curve in Figure 2.8. The dotted line is the *predicted* volume according to Charles' Law and the solid line indicates how the actual volume of the specimen will change. Calculations involving Charles' Law and other gas problems are given in Chapter XXVI.

Compression of Air. It is of value to learn the changes which take place when air or other gas is compressed. The first thing observed is that the gas becomes hot, as everyone knows who has

molecules do not behave in this way unless they are condensing to a liquid. In the gas state they collide and separate, over and over, having a higher velocity just before and after each collision and a somewhat lower average velocity between collisions. As a gas is compressed the molecular collision rate increases. The molecules spend a greater percentage of their time moving at a high velocity just before and after collisions, and a smaller percentage of their time in the slower movement between collisions, on the average. In other words, the average molecular velocity increases, which means the temperature rises.

Liquids from the Air. In the case of the major components of the air (nitrogen and oxygen) this increase in temperature is all one would observe if the air were compressed at ordinary temperatures, even though the pressure were made exceedingly high. But now if the air were cooled under very high pressure, certain characteristic temperatures would be reached, $-118.82^{\circ}\text{C}.$ for oxygen and $-147.17^{\circ}\text{C}.$ for nitrogen, at which these gases would change to liquids. At the liquefying temperatures the molecular velocity becomes so low that the molecules do not escape from one another after collisions in quite the same manner as gas molecules. They remain virtually in contact, in the liquid state, but are nevertheless free to move around through the liquid. This freedom of molecular movement gives liquids their fluidity, or lack of a fixed shape, so that they take the shape of the part of the container which they occupy.

The highest temperature at which a gas can be liquefied is known as its *critical temperature*, and the pressure which must be applied to cause liquefaction of the gas at that temperature is called its *critical pressure*. The gas, of course, also liquefies at temperatures lower than the critical temperature; the pressure then required is less than the critical pressure.

These points can be illustrated with water vapor. The critical temperature of this substance is $374.4^{\circ}\text{C}.$, which means that at any higher temperature, such as $375^{\circ}\text{C}.$, liquid water cannot be formed from steam, no matter what the pressure. The critical

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pressure of water vapor at 374.4°C. is 217.72 atmospheres (one atmosphere = 760 mm.). Now note in Table 2.2 how the pressure necessary for liquefaction drops with temperature.

TABLE 2.2 **Water Vapor Pressure for Liquefaction at Various Temperatures**

<i>Temperature of water vapor</i>	<i>Pressure required to form liquid water</i>
375°C.	Impossible to liquefy
374.4°	217.72 Atmospheres
222°	25 “
179°	10 “
133°	3 “
100°	1 “ (760 mm.)
46°	0.1 “

A gas at a temperature below its critical temperature is known as a vapor; above this temperature it is a gas.⁴ Only vapors can be liquefied, therefore. Now it is apparent why we speak of water vapor in the air, but of oxygen or nitrogen gas, at ordinary temperatures.

Boiling Point. It can be seen from the table above why water boils at 100°C., at one atmosphere pressure. When this temperature is reached the vapor pressure of the water begins to exceed atmospheric pressure, and bubbles of steam appear and rise through the liquid. It is this formation of vapor *within* the liquid which is known as boiling. The boiling point of a liquid, then, is *the temperature at which the vapor pressure of the liquid just exceeds the pressure being exerted on the liquid by the atmosphere or any other gas*. While the pressure on boiling liquids is usually close to one atmosphere, it does not have to be, and liquids can be made to boil at widely different temperatures if pressure is made very low or very high.

⁴ However, it is common usage to limit the term vapor to molecules given off by substances which can exist as stable liquids or solids under room conditions, e.g., water vapor, alcohol vapor. Under this definition carbon dioxide, ammonia, sulfur dioxide, and other substances are called gases, although they are below their critical temperatures at room conditions.

Expansion and Cooling of Gases. When the pressure is lowered on a compressed gas it expands and becomes cooler, for the reasons given earlier, but in reverse order. This furnishes us with one of our chief methods for obtaining low temperatures.

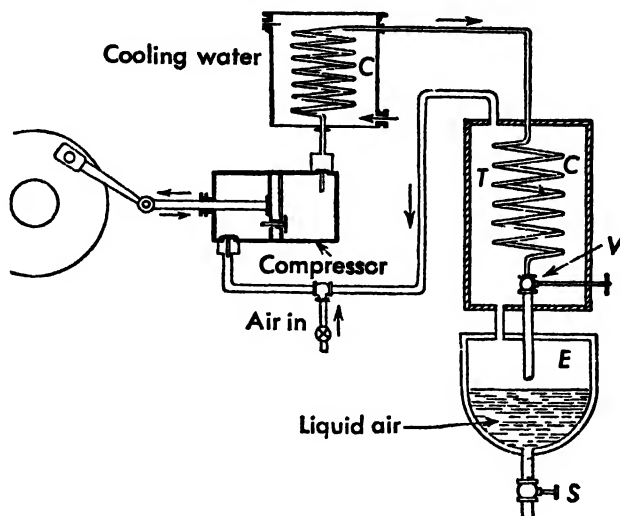


FIGURE 2.9. Apparatus for Liquefying Air. After being compressed, air is cooled at *C*, and escapes at *E*, being very cold as the result of a two hundred fold expansion at valve *V*. The cold air passes into *T*, further cooling the compressed air, then returns to the compressor. Air at *E* hence becomes colder and colder, and eventually liquefies. From Ehret, et al., *Physical Science*. Copyright, by The Macmillan Company

A compressed gas is cooled, then allowed to expand, whereupon it cools further. The important liquid air industry has been established by using this principle in a continuous manner. Compressed air is cooled by allowing it to expand, and the cool expanded air then flows around the pipes containing the compressed air, cooling it further. When this air in turn expands it therefore becomes still cooler, etc. A continual drop in temperature takes place until the air liquefies (Figure 2.9).

Solids from the Air. When liquid air is allowed to evaporate under reduced pressure, or is cooled with liquid hydrogen or helium, a drop in temperature takes place until solid air components begin to form. Thus, liquid oxygen gives pale blue,

snow-like crystals at $-218.4^{\circ}\text{C}.$, while liquid nitrogen forms colorless crystals at $-209.8^{\circ}\text{C}.$ Carbon dioxide changes to the familiar dry ice. This does not melt when put in air under ordinary room conditions because rapid formation of carbon dioxide vapor produces so much cooling that the solid remains at $-79^{\circ}\text{C}.$, over 20° below its melting point. The transition from the solid state directly to the vapor state without formation of the liquid state is known as *sublimation*.

In solid forms of matter there is no significant translational movement of molecules, since each one is fixed in space, as described earlier, but is able to vibrate around that point. This lack of translational movement of the molecules causes solids to have rigidity and a fixed shape.

AIR CONDITIONING

Human beings are most comfortable and efficient when the air temperature around them is in the neighborhood of $21^{\circ}\text{C}.$ ($70^{\circ}\text{F}.$), and the air is approximately half saturated with water vapor. The process of treating air so that it approaches or reaches this state is called *air conditioning*. The term also includes the cleaning of air. It is used, too, for industrial air processing where other conditions, such as extreme wetness or dryness, must be maintained in the making or handling of certain items. The temperature regulation of air presents no great difficulties, since it can readily be heated or cooled, but humidity adjustment is more of a problem.

humid

Relative Humidity. Before discussing humidity control the term relative humidity should be defined. Most simply, relative humidity is the actual weight of water vapor present in a given specimen of air, divided by the weight that could be present if the air were saturated, all expressed as a per cent. For example, if the air in a room could contain 300 grams of water at saturation, while it actually did contain 60 grams, it would be classed as rather dry, with a relative humidity of 20 per cent. Relative humidity can also be calculated from water vapor pressures, since the latter are proportional to the amounts of water present.

Thus, the saturation pressure of the water vapor in the air at 21°C. is 18.7 mm. If the air in a room at this temperature had a water vapor pressure of 11.2 mm., the relative humidity would be $(11.2)(100)/(18.7)$ or virtually 60 per cent. Problems dealing with relative humidity are given in Chapter XXVI.

Relative humidity is determined by using two thermometers, one dry and the other in contact with evaporating water on a wick (wet bulb). The wet bulb thermometer reads lower than the dry bulb because it is cooled by the evaporating water. The wet bulb temperature is the same as that of the dry bulb when the relative humidity is 100 per cent because there is then no water evaporation. The lower the relative humidity the faster the evaporation, the more the cooling and the greater the temperature difference between the two bulbs, as shown by the data in Table 2.3. Tables of this sort must of course first be established by using air samples with known water contents determined by a different method.

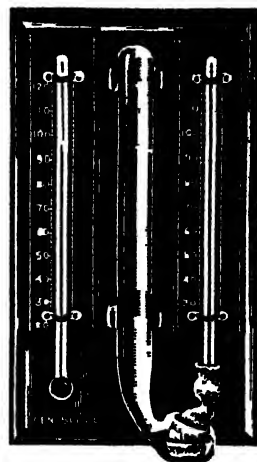


FIGURE 2.10. A Wet and Dry Bulb Thermometer. Courtesy Central Scientific Company.

TABLE 2.3 Relative Humidity from Wet and Dry Bulb Temperatures

<i>Wet bulb reading</i>	<i>Dry bulb reading</i>	<i>Relative humidity</i>
63°F.	63°F	100%
58	63	75%
55	63	59%

Humidity Control. The problem of keeping water vapor in a building at approximately the half saturation point is complicated by the temperature and relative humidity of the external air. In winter, even though the cold air outside is saturated with water vapor, it nevertheless has a low partial pressure of this substance. Thus, at the freezing point saturated air has a water vapor pressure of only 4.6 mm. If this air is brought into

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the house and warmed to 21° the water vapor pressure is still only about 5 mm., while the saturation value at 21° is 18.7 mm. The relative humidity is therefore under 30 per cent, and the air is too dry. At temperatures of the outside air below the freezing point the situation becomes worse, and winter air during a cold wave has so little water vapor in it that furniture cracks, skin becomes too dry, and an irritation may develop in the mucous membrane of the nose. This is overcome by humidifying the air, but it must be a continuous process, because of loss of water vapor through windows and doors and by condensation on cold surfaces, for example as frost on window glass.

In the summer the humidity may be too high, and if warm air is brought into the house and cooled this condition becomes worse. The familiar phenomenon of water condensing on and dropping from cold water pipes is a result of such humidity.

Air is effectively conditioned for humidity by passing it through a spray of water whose temperature is adjusted to the proper point. Air cannot only be moistened by this process, but also partially dried. The drying is accomplished by lowering the temperature of the spray water. Thus hot, overhumid air can be passed through water at 50°F. , whereupon the latter will remove water down to the saturation value at 50°F. (9.2 mm.). When this air is later warmed to 70°F. (saturation water vapor pressure, 18.7 mm.) it is seen to be close to the desired state of half saturation.

Self Study Questions

1. State the laws of Boyle and Charles. Illustrate each with an example, using an imaginary gas volume.
2. Give evidence based upon your own observation that air molecules are far apart and in motion.
3. How do we account for gas pressure in terms of molecular motion?
4. Explain how pressure is measured with a barometer. How does it happen that length units are used in measuring pressure?
5. Explain why air pressure drops as we ascend from the earth's surface.

9. A room contains 1000 cubic feet of air at one atmosphere pressure. Assuming no temperature change, what must the pressure become to cause this much air to shrink in volume to 10 cubic feet?

21. How is the humidity of the air most commonly regulated in air conditioning units? How can a spray of water partially dry the air?

III

Chemistry of the Elements and Compounds in the Air

The reader now has some fundamental knowledge of the structures and types of motion of air molecules, and is acquainted with some of the consequences of each. This information is not as typically chemical in nature as that to be presented in the following chapter, since it lies more in the region between physics and chemistry. Nevertheless, it is basic to a true understanding of chemistry.

Let us now consider the chemistry of the different types of air molecules. It is usually customary, in teaching the chemistry of a substance, to proceed by describing, in turn, its occurrence, a little about its discovery, its preparation, properties, and uses. Along with this specific information there may also be introduced new laws or terms or theoretical concepts of a general nature which can be conveniently illustrated by the behaviour of the substance in question. This procedure will in general be followed here, and if the reader will keep this in mind he will be better able to organize his studying.

✓ OXYGEN

While oxygen, like the other substances discussed in this chapter, is present in the air, this is not its chief occurrence. Oxygen is found mainly in the earth's crust, and makes up about half of the latter. For example, common minerals like quartz (SiO_2), calcite (CaCO_3), the feldspars (such as KAlSi_3O_8)

and hundreds of others are high in oxygen content. Oxygen also comprises nearly 90 per cent of water (page 40), and, too, it is part of nearly all of the molecules which are found in living organisms.

When an element occurs in compounds along with other elements, as oxygen in these substances, it is said to be present in *combined form*. On the other hand, when it occurs uncombined, like oxygen in the air, it is said to be *free*.

Oxygen was first recognized as a distinct substance by Scheele (Sweden) and Priestley (England) in the period from 1770 to 1775. They prepared the element by heating various decomposable substances which contained it, such as mercuric oxide.

Preparation. Oxygen is obtained industrially from liquid air,¹ and by electrolysis (page 135) of water. In the laboratory it is usually made by heating potassium chlorate, KClO_3 . The chemical reaction which takes place is known as a decomposition. The chemist shows the change in an abbreviated form by writing a *chemical equation*,



FIGURE 3.1. Industrial Preparation of Oxygen. Distillation unit in a plant which yields 200 tons of 90 per cent pure oxygen per day from liquid air. This plant requires as raw material more than 5 million cubic feet of air an hour. Courtesy The Linde Air Products Company.

¹ When air is liquefied and allowed to boil, nitrogen comes off as a gas at -195°C . When the remaining liquid is warmed to -183°C ., oxygen then boils off. A separation of fairly pure nitrogen and oxygen can be brought about in this manner from liquid air. The process is called fractional distillation.

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usually called simply an equation. The arrow after oxygen means that this substance is liberated as a gas.

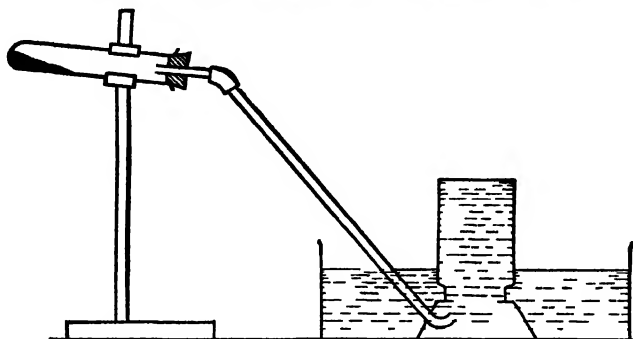


FIGURE 3.2. Laboratory Preparation of Oxygen. The mixture of potassium chlorate and manganese dioxide at the left is heated, yielding oxygen gas which displaces water from the inverted wide mouth bottle at the right. From Brinkley, *Principles of General Chemistry*, Fourth Edition. Copyright, 1951, by The Macmillan Company.

K is the symbol for potassium and Cl for chlorine. Equations must be balanced, like the nuts and bolts example on page 10, and a brief inspection of the one just written shows that it is not, since there are three oxygen atoms on the left and but two on the right. The equation could be balanced by changing the formula of potassium chlorate.



But this is not a permissible procedure because formulas of substances are fixed by nature, i.e., there are actually three oxygen atoms for each potassium and chlorine atom in potassium chlorate; this fundamental fact is not altered by writing the composition otherwise.

Leaving the formula as KClO_3 , let us then balance the equation by writing one and a half molecules of oxygen on the right.



The equation is again balanced, with three oxygen atoms on each side. Equations having fractional coefficients are occasionally

written. However, it is usually customary to employ only whole numbers, particularly if we mean the symbols to represent molecules, rather than larger quantities. Such an equation is

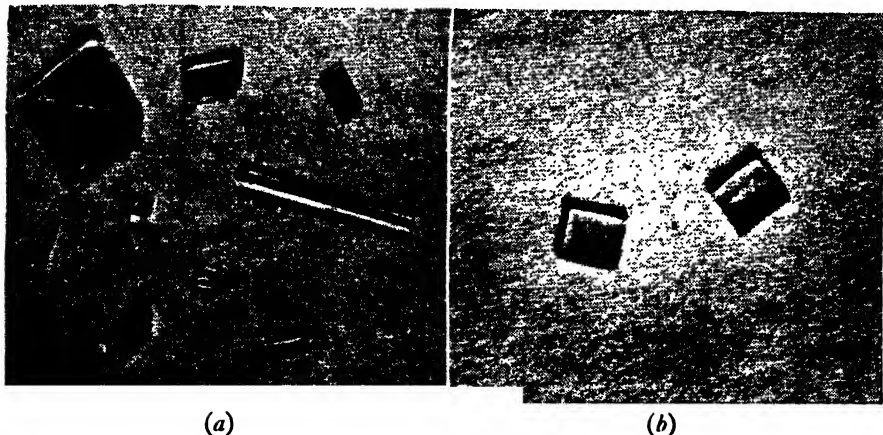


FIGURE 3.3. Crystalline Substances Used and Formed During Preparation of Oxygen. (a) Potassium chlorate, (b) potassium chloride.

readily obtained from (3) by multiplying each quantity of molecules² by two.



Catalysis. In the preparation of oxygen by this method, a much faster evolution of the gas takes place if a little manganese dioxide (MnO_2) is mixed with the potassium chlorate before heating. The manganese dioxide is not converted to anything else during the experiment, because after the decomposition is complete it can be recovered. Such substances, which change the rate of a chemical reaction without being permanently altered in the process, are known as *catalysts*.

The change in reaction rate produced by addition of a catalyst is known as *catalysis*. Most catalysts increase reaction rates, as for example in the decomposition just mentioned, or in many reactions in living plants and animals (catalyzed by enzymes). On the other hand, some catalysts are used to slow up or inhibit

² The word molecule is used loosely when applied to potassium chlorate and potassium chloride. As we shall see later, these substances are made up of ions.

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undesirable chemical changes. These are known as inhibitors or retarders. Substances added to slow up the oxidation of rubber or the corrosion of metals, for example, would fall in this category.

Properties. Chemists recognize two kinds of properties of matter. One kind impress themselves upon our senses, or upon measuring instruments, without the taking place of any chemical changes, i.e., without new molecules being formed. These are known as *physical properties*. Color, melting point, boiling point, density, and critical temperature are examples of physical properties.

The other kind of property is the ability of a substance to undergo a chemical change, that is, a change in molecular structure. This is known as a *chemical property*. It is thus a chemical property of oxygen to react with carbon at high temperatures to form carbon dioxide. Besides such specific chemical properties there are general chemical properties, involving a number of chemical changes of similar type. For example, it is a general chemical property of oxygen to react with metals and form metallic oxides. Let us consider in more detail the properties of oxygen.

Physical Properties of Oxygen. The physical properties of this element are given in Table 3.1.

TABLE 3.1 Physical Properties of Oxygen

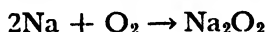
	<i>Gas</i>	<i>Liquid</i>	<i>Solid</i>
PROPERTY			
COLOR	Colorless	Pale blue	Pale blue
ODOR	None	None	None
CRITICAL TEMP.	-118.82°C.		
CRITICAL PRES.	49.713 atm.		
DENSITY (g. per l., S.C., gas, g. per cc., liquid and solid)	1.429	1.14(-183°C.)	1.426(-252.5°C.)
DENSITY RELATIVE TO AIR	1.105		
SOLUBILITY IN WATER	4.89 cc. in 100 g. water at 0°C.		
BOILING POINT		-183°C.	
MELTING POINT			-218°C.

By the density of a gas is usually meant the weight of one liter at standard conditions ($0^{\circ}\text{C}.$ and 760 mm. pressure). This is 1.429 grams in the case of oxygen. The density relative to air means the weight of a given volume of a gas divided by the weight of the same volume of air, e.g., oxygen is 1.105 times as dense as air. Both gases must be at the same temperature and pressure in making this comparison. The liquid and solid densities of oxygen mean the weight in grams of one cubic centimeter of these substances. Since this varies with temperature, the latter must be stated for greatest accuracy.

The physical properties of oxygen can be summarized in a sentence, without use of numerical data, by saying it is a colorless, odorless gas, rather difficult to liquefy, slightly heavier than air and slightly soluble in water.

Chemical properties of oxygen. The chemical properties of oxygen can be summarized by saying it reacts with most metals and with many nonmetals and compounds. Let us consider examples of each type.

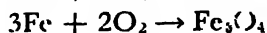
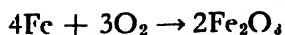
If the proper reaction temperature is chosen, oxygen acts upon nearly all of the metals. For example, it combines with metallic sodium to form sodium peroxide, Na_2O_2 .



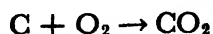
Calcium reacts with oxygen to form calcium oxide.



Iron forms two different oxides, one at high temperatures, magnetic oxide of iron (Fe_3O_4), the other at low temperatures, rust (Fe_2O_3). Water is also present to a variable extent in iron rust.

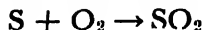


Oxygen also reacts with many nonmetals. The burning of carbon (charcoal, coke) is a familiar example. With an excess of oxygen carbon dioxide is formed.



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Sulfur forms sulfur dioxide at elevated temperatures.

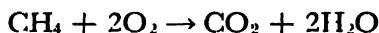


Phosphorus burns with an excess of oxygen to form a smoke consisting of white, solid particles of P_4O_{10} .

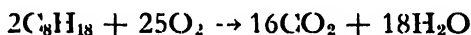


Note the new symbols: Na (sodium), Ca (calcium), Fe (iron), S (sulfur), P (phosphorus).

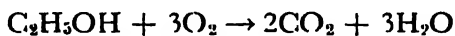
Oxygen also reacts with many compounds, most of which contain carbon. Thus, methane, the chief component of natural gas, burns according to the following equation:



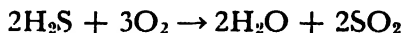
Gasoline molecules burn similarly if supplied with enough oxygen. The octane molecule of gasoline, for example, reacts as follows:



Alcohol burns with a blue flame:



A compound does not necessarily have to contain carbon before it will react with oxygen. Thus, hydrogen sulfide burns in oxygen:



Oxidation; Combustion. Reactions in which oxygen combines with some other substance are in general called *oxidations*. However, this term also has a more general meaning which will be described later (page 263). Oxidations take place at different rates. The rusting of iron, or the decaying of dead wood or fallen leaves, are examples of slow oxidation. On the other hand oxidations at elevated temperatures are often fast processes. When a rapid oxidation is accompanied by emission of light and obvious heat it is called *combustion*, or *burning*. Flames, caused by burning of emitted gases, are frequently characteristic of combustion, but not always. These rapid oxidations do not take place until

there has been a certain minimum elevation of temperature, reaching what is known as the *kindling temperature*. The use of such things as matches and cigarette lighters to produce kindling temperatures is familiar to all.

When a reaction is accompanied by the emission of heat it is called *exothermic*. Most chemical changes are of this type, e.g., the burning of coal in a furnace. However, heat is absorbed during some reactions, in what is known as an *endothermic* change.

Spontaneous Combustion. Materials undergoing a slow oxidation may have so much dead air space that the insulation prevents effective dissipation of the heat generated. Under these conditions the rise in temperature may be such that the kindling point is reached, whereupon the mass bursts into flame. This type of combustion, which starts of its own accord, is known as *spontaneous combustion*. Hay and coal piles have been known to so ignite. A particularly dangerous hazard in this respect is a pile of rags wet with drying oils, such as may result from cleaning paint brushes. Oxidation of the oil may lead to spontaneous combustion.

Chemical Formulas of Binary Oxides. Most of the formulas of the metallic and nonmetallic oxides just mentioned can be reasoned out if the valences (page 35) of the elements are known. The two elements will be present in sufficient amount to account for equal valences, i.e., the valence *per atom*, times the number of that kind of atom in the molecule, will be the same for the two elements. In carbon dioxide, for example, carbon has a valence of four and oxygen of two. Hence two oxygen atoms must combine with one carbon atom to give each element a total valence of four. However, this simple rule in its present form holds only for binary compounds (those containing but two kinds of elements), and even here there are exceptions, such as Fe_3O_4 and Na_2O_2 , in which the rule fails to render easy assistance, either because an element is exhibiting two valences in the same molecule (as the iron in Fe_3O_4), or because like atoms are joined together (as the oxygen in Na_2O_2). Later on an extension of this

same rule will be of great assistance in working out formulas for acids, bases, and salts (page 161)

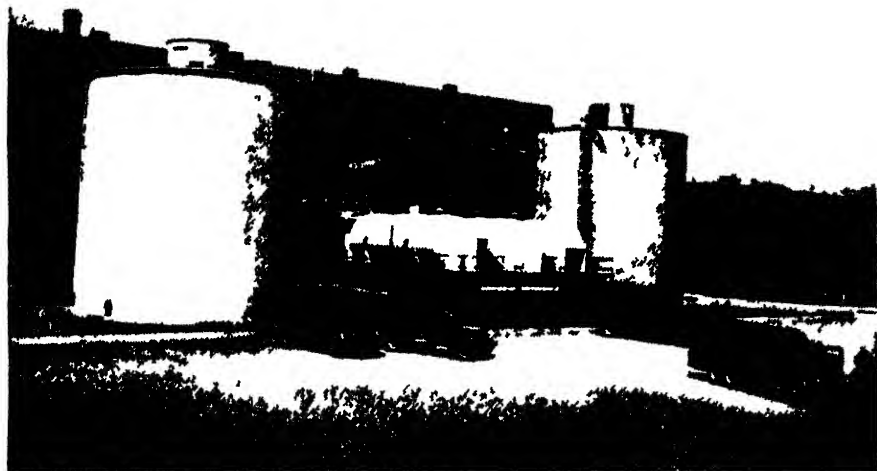
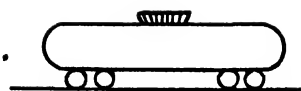
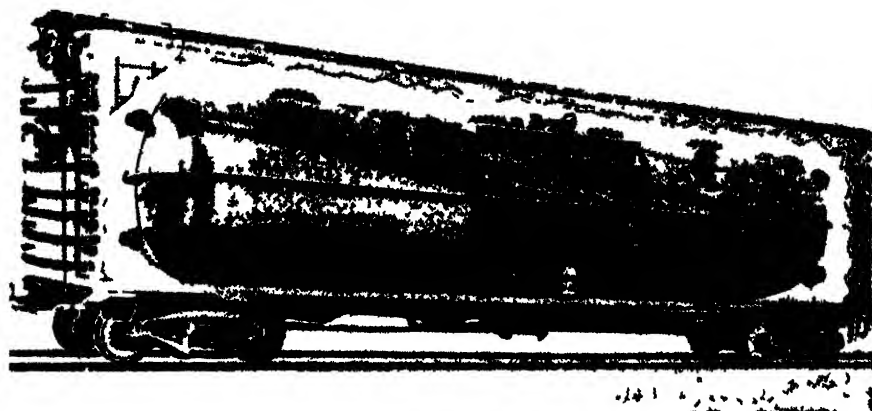


FIGURE 3 4 Liquid Oxygen Storage Tanks The large tanks hold the gaseous equivalent of 25 million cubic feet of oxygen each, the small tanks 1 5 million cubic feet If these tanks held oxygen gas at standard conditions they would need to be 900 times as large Courtesy The Linde Air Products Company

Uses of Oxygen. Life as we know it would be impossible without oxygen, since this element is needed by animals, and to a more limited extent by plants, to burn up food products and thus to furnish the energy necessary for the maintenance and propagation of life. It is also necessary for burning the fuel which keeps us warm, cooks our food, runs our machinery, etc. Besides these uses which require the diluted form of oxygen which we know as air, pure oxygen has many uses. It is employed to enrich the air given to people with impaired respiration, such as pneumonia patients. It is used similarly in high altitude flying. Oxygen is employed to give a mixture with acetylene gas which burns with a very hot flame. This is used (blowtorch) for welding and cutting iron and steel. A mixture of oxygen and hydrogen is also utilized for welding. In some steel mills oxygen is now added to enrich the air used in the metallurgical operation of converting pig iron into steel, in this way shortening the process.



1-tank car of liquid oxygen

=

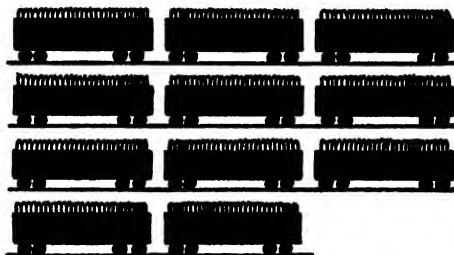
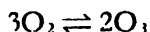
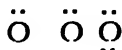
11 railroad cars of cylinders
or
3100-cylinders-150 lbs each

FIGURE 35 Tank Car for Transporting Liquid Oxygen. A great saving is effected by shipping liquid oxygen rather than gaseous oxygen. Courtesy The Linde Air Products Company.

Ozone. In the upper atmosphere ultraviolet radiation from the sun is thought to cause a change in the composition of the oxygen molecule from two atoms of oxygen to three



The substance formed, ozone, is chemically much more active than ordinary oxygen. It probably has the electron structure shown below



Ozone is also formed from oxygen when a silent electrical discharge takes place between two charged surfaces. It is commonly

made in this way. In general, the absorption of electrical energy or ultraviolet radiation by diatomic oxygen at low temperatures leads to the formation of ozone.



FIGURE 3.6. An Important Use of Oxygen. This bar-cutting machine employs oxyacetylene flames. Courtesy The Linde Air Products Company

Ozone is pale blue as a gas, deep blue as a liquid. The gas has a characteristic odor. Chemically it behaves similarly to oxygen but more vigorously, because of its higher energy content. It is used in bleaching, deodorizing and disinfecting, since it oxidizes many colored substances to colorless ones, odorous substances to odorless ones, and kills bacteria. At comparable pressures ozone is much more soluble in water than is oxygen.

Reversible Reactions. In the equation for the formation of ozone, the arrows are seen to point in both directions. This is the way in which the chemist indicates a *reversible* reaction, that is, one that can be made to go in either direction, depending upon the conditions. In such systems, when the rate of chemical change in one direction is the same as the rate in the other direction, so that no apparent change is taking place, a state of *chemical equilibrium* is said to be reached. However, by changing conditions one of these reactions can be made to take place more rapidly than the other, thus temporarily destroying the equilib-

rium. The presence of electrical or ultraviolet energy and a low temperature favors the formation of ozone from oxygen, while in the absence of these and at higher temperatures the reverse change tends to take place.

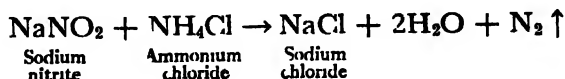
Theoretically, at least, all reactions should be reversible to some extent, but in practice the term is usually restricted to those chemical changes in which the reversibility can be shown experimentally, i.e., in which the presence of the starting substances and of the products can be demonstrated under equilibrium conditions.

NITROGEN

Occurrence. The chief occurrence of nitrogen is in the air, there being some 20 million tons of the free element over each square mile of the earth's surface. Nitrogen also occurs in combined form as sodium nitrate, chiefly in Chile (Chile saltpeter). Many of the molecules which make up plants and animals likewise contain nitrogen. The largest of these, the *proteins*, are giant molecules consisting of many carbon, hydrogen, oxygen, nitrogen, and often sulfur atoms and others. However, the quantity of free nitrogen in the air far outweighs all combined nitrogen.

The early work of Rutherford, Scheele, and Lavoisier about the time of the American revolution resulted in the recognition of nitrogen as a separate element. It was first named azote (Lavoisier), but later called nitrogen (Chaptal) because it was a constituent of niter (potassium nitrate).

Preparation. Nitrogen, like oxygen, is prepared on a large scale from liquid air. When the latter is distilled the nitrogen comes off first, leaving the oxygen behind (compare boiling points). When it is desired to make small amounts of nitrogen in the laboratory the method generally employed is to mix saturated solutions of sodium nitrite and ammonium chloride.



Physical Properties of Nitrogen. The physical properties of nitrogen are given in Table 3.2.

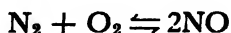
TABLE 3.2 Physical Properties of Nitrogen

	<i>Gas</i>	<i>Liquid</i>	<i>Solid</i>
PROPERTY			
COLOR	Colorless	Colorless	Colorless
ODOR	Odorless	Odorless	Odorless
CRITICAL TEMP.	-147.17°C.		
CRITICAL PRESS.	33.46 atm.		
DENSITY (g. per l., S.C., gas, g. per cc., liquid and solid)	1.251	0.808(-195.8°C.)	1.026(-252.5°C.)
DENSITY RELATIVE TO AIR	0.967		
SOLUBILITY IN WATER	2.35 cc. in 100 g. water at 0°C.		
BOILING POINT		-195.8°C.	
MELTING POINT			-210°C.

In summary, nitrogen is a colorless, odorless gas, difficult to liquefy, slightly lighter than air and slightly soluble in water. Note that the solubility of nitrogen in water is only about half that of oxygen.

Chemical Properties of Nitrogen. In its chemical behaviour, nitrogen combines with other substances far less readily than oxygen. If this were not the case, i.e., if the nitrogen in the air were as reactive as the oxygen, life on the earth would have to be considerably modified. Fires would burn fiercely, and would be difficult to control. Living creatures with their present respiration rate would very rapidly burn up ingested food, and all oxidations would take place much faster. As it is, nitrogen acts as a diluent for the more active oxygen.

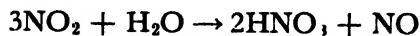
Nitrogen takes part in a few chemical changes in nature. During electrical storms it combines to a slight extent with oxygen in a reaction activated by lightning. The gas *nitric oxide*, NO, is formed.



This then takes on more oxygen to yield the brown gas *nitrogen dioxide*, NO_2 .



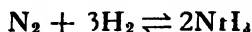
and this in turn reacts with water present in the air to form *nitric acid*, HNO_3 .



The nitric acid is carried to earth as an exceedingly dilute solution by falling rain during thunderstorms. Combined nitrogen in soluble form is needed for the successful growth of plants, and this is one way in which they get it.

Fixation of Nitrogen; Ammonia. The conversion of atmospheric nitrogen to compounds of the element is called the *fixation* of nitrogen; the process just described is one of nature's ways of doing this. Nitrogen is also fixed by nature in another, more important way. Certain types of plants such as peas, beans, alfalfa, and clover (legumes) have swollen places on their roots, called nodules, which house nitrogen-fixing bacteria. The latter convert atmospheric nitrogen directly into nitrogen compounds as part of their life process. Plants containing these bacteria are often grown to increase the nitrogen content of the soil.

Man brings about the fixation of nitrogen in an important industrial process which yields ammonia. Nitrogen gas and hydrogen gas are heated under pressure, and in the presence of a catalyst.



Ammonia is recovered as a liquid, at the high pressure employed, from this equilibrium mixture. It is one of our important chemicals, manufactured to the extent of over a million tons yearly. The reader is familiar with its aqueous solution used in the home (household ammonia). In somewhat stronger solutions this is also a common laboratory reagent, often called ammonium hydroxide (page 159). Much synthetic ammonia is employed in the manufacture of nitric acid (page 155), which in turn finds wide use in the manufacture of explosives, plastics, dyes, and drugs.

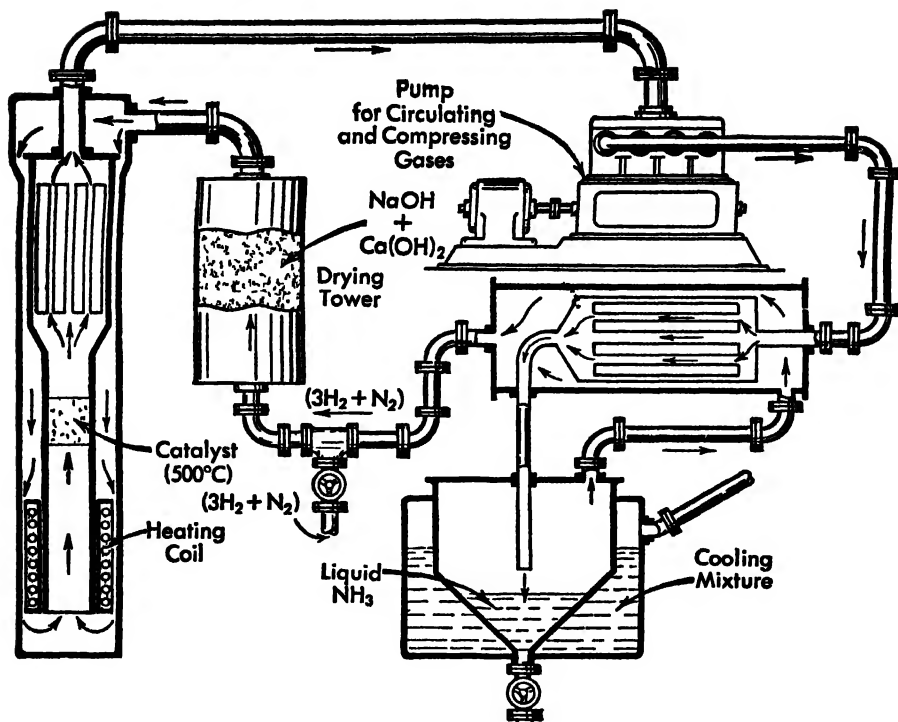
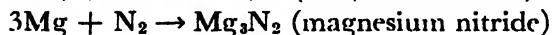


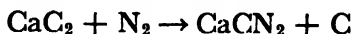
FIGURE 3.7. Preparation of Ammonia from Nitrogen and Hydrogen. Nitrogen and hydrogen gases enter at lower left center. These combine in part to form ammonia, which is liquefied and collected at lower right. The uncombined gases return to the catalyst at left and go through the system again and again until converted to ammonia. From Sisler, Vander Werf and Davidson, *General Chemistry: A Systematic Approach*.

Nitrogen also reacts with certain metals to form *nitrides*. Thus, when magnesium burns in the air, it is partly converted to magnesium oxide and partly to magnesium nitride.



Uses of Nitrogen. Besides the natural uses of nitrogen in the air as an oxygen diluent and as a source of fixed nitrogen, the nearly pure substance from liquid air is employed in large quantities in the preparation of ammonia, mentioned above. It is also

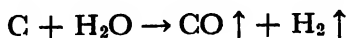
commonly used whenever a cheap, inert gas is needed to fill a region where oxygen is to be excluded because of its reactivity, as over the mercury in thermometers, or in light bulbs. It is employed in the manufacture of calcium cyanamide, an important intermediate chemical, from calcium carbide.



HYDROGEN

Occurrence. Only traces of free hydrogen occur in the air, and even the combined hydrogen in water vapor makes up only a very small fraction of the total air mass. The chief occurrence of hydrogen is in liquid water and ice. Besides this, it is present in a great many carbon compounds, including those in natural gas and petroleum, and also in the proteins, carbohydrates, and fats associated with living things. Vast quantities of hydrogen occur in the sun and stars. Cavendish (English) was probably the first scientist to recognize hydrogen as a distinct substance in 1766. He called it "inflammable air," and the name hydrogen was suggested later by Lavoisier.

Preparation. Hydrogen is prepared industrially by passing steam over hot coke or iron. If coke (carbon) is used, the products are carbon monoxide and hydrogen. This mixture, known as *water gas*, is an important industrial fuel. When hydrogen is



the desired product the carbon monoxide is removed by oxidiz-

ing it to carbon dioxide and dissolving it in water under pressure

If iron is used, relatively pure hydrogen is obtained.

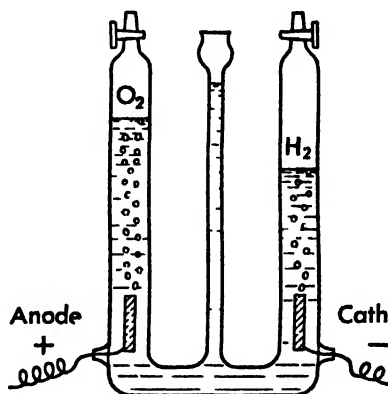
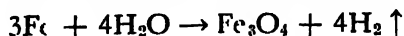
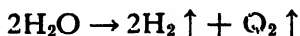


FIGURE 38. Laboratory Preparation of Hydrogen and Oxygen by Electrolysis From Ehret, et al., *Physical Science*. Copyright, 1942, by The Macmillan Company.

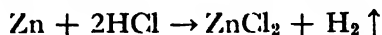
82 **The Atmosphere**

The iron can be regenerated from the iron oxide by use of water gas, and can thus be used over and over again.

Hydrogen is also made industrially by the electrolysis of water. Electrolysis will be explained later (page 135); for the present it is sufficient to know that when electricity is passed through a water solution of certain conducting substances, the water is broken up into its constituent elements.



In the laboratory hydrogen is commonly prepared by the action of hydrochloric acid upon zinc. Hydrogen is evolved and the



colorless, crystalline product zinc chloride can be recovered after evaporation of the solution. The chemical change here is a type known as a *displacement*, in which element I in the free state reacts with a compound of element II, with the result that element II becomes free and element I forms a compound. Displacements most often involve metals and hydrogen and their compounds. A more fundamental explanation of the process is possible in terms of ions and electron transfer from zinc to hydrogen, but this will be postponed until the reader has studied the chapter on ionization and the section on the activity series (pages 143, 229).

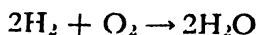
Physical Properties of Hydrogen. Some important physical properties of hydrogen are given in Table 3.3.

TABLE 3.3 Physical Properties of Hydrogen

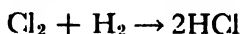
	<i>Gas</i>	<i>Liquid</i>	<i>Solid</i>
PROPERTY			
COLOR	Colorless	Colorless	Colorless
ODOR	Odorless	Odorless	Odorless
DENSITY (g. per l., S.C., gas, g. per cc., liquid)	0.08987	0.0709 (−252.7°C.)	
DENSITY RELATIVE TO AIR	0.06948		
CRITICAL TEMP.	−239.9°C.		
CRITICAL PRESS.	12.8 atm.		
BOILING POINT		−252.7°C.	
MELTING POINT			−259.1°C.
WATER SOLUBILITY	2.1 ml. in 100 g. water at 0°C.		

In summary, hydrogen is a colorless, odorless gas, slightly soluble in water, very difficult to liquefy and having the lowest density of any substance.

Chemical Properties of Hydrogen. Hydrogen reacts with many nonmetals, with some compounds, and with certain metals. Thus, hydrogen combines explosively with oxygen when a mixture of the two gases or a portion thereof is heated to 700°C.



Hydrogen chloride forms similarly and at lower temperatures in the presence of bright light such as sunlight.

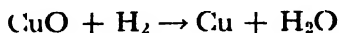


The combination of hydrogen and nitrogen (page 79) is another example of hydrogen reacting with a nonmetal.

Hydrogen combines with certain unsaturated compounds of carbon to form saturated compounds, meaning substances which will not take up further hydrogen. Thus, with ethylene, hydrogen reacts to form ethane.



An important general chemical property of hydrogen is its ability to react with many metal oxides to form water and the metal. This process—the *removal* of oxygen from a compound—is known as *reduction*. The term, like oxidation, also has a more general meaning which will be discussed later. Hydrogen reacts with copper oxide, for example, reducing the latter to free copper.



Uses of Hydrogen. Because of its low density, hydrogen is used to fill lighter-than-air craft, such as balloons and dirigibles.

However, a fire hazard is always present when this gas is used, and helium, with nearly as great lifting power, is preferred whenever it can be obtained, because of its chemical inertness.

Hydrogen finds important uses in the chemical industry. It is one of the reacting substances in the preparation of ammonia,

methyl alcohol, formaldehyde and the solid, edible fats made by hydrogenating liquid fats such as cottonseed oil. If the hydrogenation of coal becomes an important industrial process this will cause a further demand for large quantities of the gas. Hydrogen is also used in obtaining certain metals from their oxides. Tungsten is so made. The oxygen-hydrogen blowtorch, mentioned earlier, provides another use for hydrogen.

CARBON DIOXIDE

Occurrence. Carbon dioxide is a minor component of the atmosphere, but highly important nevertheless as a necessary molecule for plant growth (page 85). An average of about three carbon dioxide molecules is present per 10,000 air molecules. This average remains constant³ because the gas is formed and used up at about the same rate, i.e., the amount absorbed by plants and by water is about the same as that liberated during decay, respiration, the burning of carbon and its compounds, etc. Carbon dioxide was probably first recognized as a distinct substance about 350 years ago by the Belgian scientist Van Helmont.

Preparation. Carbon dioxide is formed when carbon, or any organic compound of carbon, is heated with sufficient oxygen. Examples of such oxidations are given on page 72. Many metal carbonates lose carbon dioxide when heated, as for example the calcium carbonate present in limestone. The products in this case are quicklime and carbon dioxide.



It forms, too, when these same carbonates are treated with acids. With hydrochloric acid, for example:



Carbon dioxide is also given off during the fermentation of sugar to alcohol (Chapter XV).

³ Constant, that is, during this period of the earth's history. There is some evidence that the carbon dioxide content of the atmosphere used to be higher than it is today.

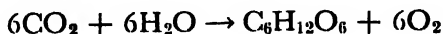
Physical Properties of Carbon Dioxide. Important physical properties of this substance are shown in Table 3.4.

TABLE 3.4 Physical Properties of Carbon Dioxide

	<i>Gas</i>	<i>Liquid</i>	<i>Solid</i>
PROPERTY			
COLOR	Colorless	Colorless	Colorless
ODOR	Odorless	Odorless	Odorless
DENSITY (g. per l., S.C., gas, g. per cc., liquid and solid)	1.98	1.101(−37°C.)	1.56(−79°C.)
DENSITY RELATIVE TO AIR	1.53		
CRITICAL TEMP.	31.35°C.		
CRITICAL PRESS.	72.9 atm.		
MELTING POINT			sublimes at −79°C.
BOILING POINT			
SOLUBILITY IN WATER	one volume gas in one volume water at 15°		

In summary, carbon dioxide is an odorless, colorless gas, fairly soluble in water, easy to liquefy, but not existing as a liquid at ordinary pressures, since it sublimates directly from the solid to the gas state.

Chemical Properties of Carbon Dioxide. The most important chemical change which carbon dioxide undergoes is that which takes place in the leaves of plants (photosynthesis). Sugar⁴ and oxygen are formed from carbon dioxide and water, although not in one step as shown.



Without this fundamental change life as we know it could not exist, since it is necessary for the plant growth upon which animal life depends.

Carbon dioxide also reacts with water to form the substance *carbonic acid*, H_2CO_3 .



⁴ Some authorities prefer to say "organic matter" rather than sugar, because, while sugar is eventually formed, it may not be the first product of the reaction.

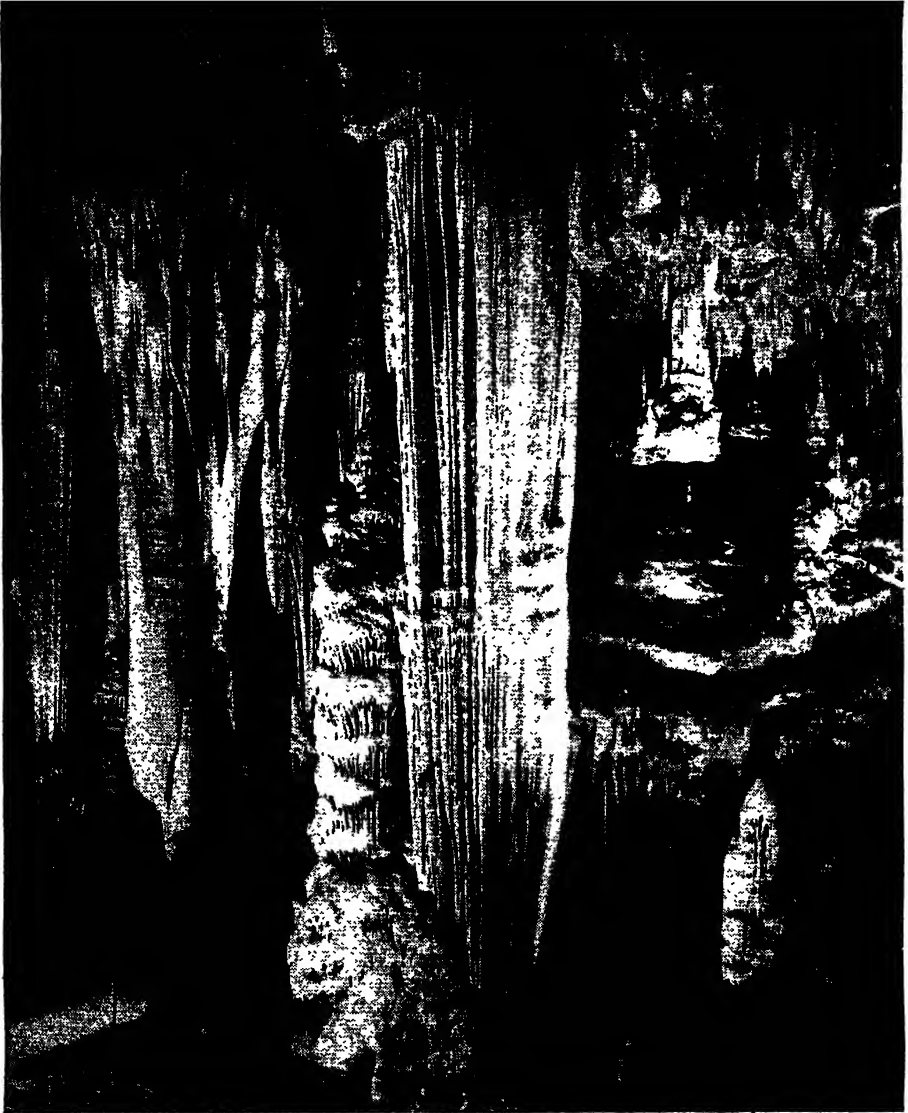
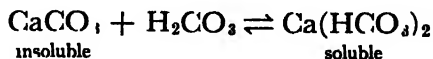


FIGURE 3.9. Interior of a Limestone Cave, Showing Stalactites and Stalagmites. Courtesy Luray Caverns Corporation.

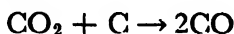
This substance exists only in dilute water solution. It gives soda water (carbon dioxide dissolved in water) its slightly sour taste. In nature, carbon dioxide solutions are formed when air containing this gas comes in contact with water. These solutions have a

dissolving action upon limestone, and in this way we account for the formation of limestone caves. Soluble calcium bicarbonate is formed from the calcium carbonate of limestone.



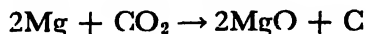
When a water solution of calcium bicarbonate evaporates, as from the roof or floor of a cave, the reaction reverses, and calcium carbonate precipitates again. We thus explain the stalactites and stalagmites found in caves.

Carbon dioxide reacts with carbon at elevated temperatures to form carbon monoxide.



Carbon monoxide is an odorless, colorless, highly toxic gas. The reaction above takes place when coal or carbon compounds in general burn with an insufficient amount of air. Carbon dioxide forms first, and in the absence of further oxygen it reacts with additional hot carbon as shown. For this reason the flue system of stoves and furnaces should be carefully checked for leaks, and in general the gases from burning carbon or its compounds should not be given the opportunity to get into the lungs. This applies particularly to the exhaust gases from automobiles.

Carbon dioxide reacts with active metals. With magnesium at elevated temperatures, for example:



Uses of Carbon Dioxide. This gas has many uses. It is required for photosynthesis. It is employed in large amounts in making carbonated beverages. It also finds use in the solid form as the refrigerant popularly known as *dry ice*. The latter has the two advantages that it is much colder than ice ($-79^\circ\text{C}.$) and it does not melt and cause a liquid disposal problem since it goes directly from the solid to the gas state at atmospheric pressure.

Large quantities of carbon dioxide are utilized in the industrial manufacture of sodium bicarbonate (NaHCO_3) from salt. While the sodium bicarbonate is of importance in itself as baking

soda, it is also the starting material from which the key industrial chemical sodium carbonate (Na_2CO_3 , soda ash) is made.

Carbon dioxide is generated, and used for leavening purposes, when baking powder is moistened. The rising of all types of

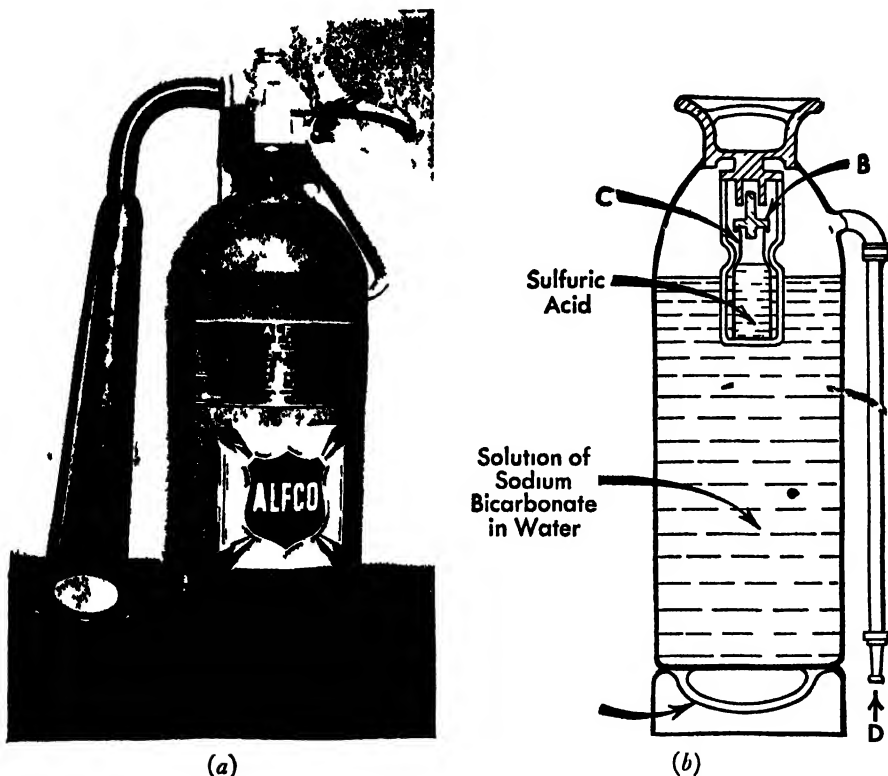


FIGURE 3 10 Uses of Carbon Dioxide (a) A liquid carbon dioxide fire extinguisher, (b) a sodium bicarbonate-sulfuric acid fire extinguisher which generates carbon dioxide when the two solutions are mixed. From Sisler, Vander Werf and Davidson, *General Chemistry, A Systematic Approach*

dough is in general caused by formation of bubbles of carbon dioxide which result from the action of yeast upon sugar, or when sodium bicarbonate and an acid substance react.

Another way in which carbon dioxide is employed is in the extinguishing of fires. A common type of fire extinguisher generates carbon dioxide, when it is inverted, by the mixing of sodium

bicarbonate solution and an acid substance, usually sulfuric acid or aluminum sulfate.

Mixtures of carbon dioxide and oxygen are used as an aid to respiration in cases of asphyxiation or respiratory infections. While the oxygen is the important gas in this mixture, the carbon dioxide appears to stimulate the nerves which control the respiratory muscles.

THE INERT GASES

Occurrence. These substances, helium, neon, argon, krypton, and xenon, occur in the atmosphere. To this list should also be added radon, which does not exist in the air but which has the proper electron configuration to be an inert gas (eight electrons in the outermost shell). Radon is radioactive, and therefore exists only a short time after its formation from radium (page 283).

Argon constitutes nearly one per cent of the air, but the remaining inert gases are present only in traces. Another, much better, source for helium is in the natural gas obtained from some Texas wells. This contains up to about one percent of helium which can be recovered by liquefying the remaining substances—a process made possible by the fact that helium has the lowest critical temperature and boiling point of any substance.

Cavendish, Rayleigh, and Ramsay (England) accumulated enough evidence between them over a period of more than a hundred years to show the existence of argon in the atmosphere. It was named in 1894. In the same year helium was found on the earth, 26 years after it had been discovered in the sun by means of the spectroscope. Neon, krypton, and xenon were found in 1898 by use of the spectroscope (Ramsay and Travers) after they had been concentrated by fractional distillation (page 67) of liquid air. The inert gases are still prepared in this way, except helium, which is obtained from some natural gas deposits as mentioned above.

Properties. Since these gases are chemically inert they undergo practically no chemical changes. Their physical properties are shown in Table 3.5.

TABLE 3.5 Physical Properties of the Inert Gases

Gas	Density	Boiling point	Critical temperature	Critical pressure
HELIUM	0.1785	-268.9°C.	-267.9	2.26 atm.
NEON	0.900	-246.0	-228.7	25.9
ARGON	1.782	-185.9	-122.4	48.0
KRYPTON	3.708	-151.8	-62.6	54.2
XENON	5.85	-109.1	16.6	58.2
RADON	9.88	-61.8	104.4	62.4

Uses. All things considered, helium is our best gas for lighter-than-air craft. Even though it has twice the density of hydrogen, its lifting power is nearly as great, since lifting power depends upon the *difference* in density between the gas and the air it displaces. This difference per liter is $(1.29 - 0.09)$ or 1.20 g. for hydrogen and $(1.29 - 0.18)$ or 1.11 g. for helium. Helium therefore has 92 per cent of the lifting power of hydrogen. In addition, helium does not burn and it has a considerably lower rate of diffusion, i.e., in the event of a leak it will not escape as rapidly as hydrogen.

Helium is sometimes substituted for nitrogen in an artificial air mixture used by deep-sea divers. When nitrogen is present in the air supplied under these pressures it dissolves in the blood. If the pressure is reduced to atmospheric too rapidly when the diver ascends, some of this nitrogen comes out of the blood and forms gas bubbles,⁵ leading to a painful condition known as the "bends." This is prevented by lowering the pressure more slowly and by replacing nitrogen with helium, since the latter gas has a very low solubility in the blood.

Large amounts of argon are now used in light bulbs. If the space around the filament is filled with this gas there is a lower heat conductance than if nitrogen were used, resulting in a greater efficiency. The inertness of the gas also helps prevent chemical changes in the filament. Other inert gases are also employed in the same manner.

Neon and other inert gases, and substances besides the inert

⁵ An illustration of Henry's Law. See page 171.

gases (such as carbon dioxide and mercury vapor) are used in the familiar neon signs. The various colors are produced by employing mixtures of gases and by varying the color and composition of the glass. Besides the brilliant light which these signs emit they have the further advantage that they operate at very low amperages, hence require but little electricity.

WATER VAPOR

The substance water will be discussed later in some detail, so but little mention of it will be made here. Water has a critical temperature of $374.4^{\circ}\text{C}.$, and a high critical pressure, 217.8 atmospheres. It is of interest to note the wide variation of water vapor content of the air that is possible in nature. At $-50^{\circ}\text{F}.$, for example, a not uncommon winter temperature in arctic regions, the saturation vapor pressure is only about 0.05 mm., meaning that there will be less than one water molecule per 10,000 air molecules. At the other extreme of $137^{\circ}\text{F}.$, the highest known air temperature caused in nature by the sun's heat, air can hold about 18 per cent water molecules, or 1800 in every 10,000 air molecules. The knowledge of this great possible variation helps to explain why heavy snowfalls are uncommon during extremely cold weather and also why tropical rains are often such deluges.

IMPURITIES IN THE AIR

That portion of the air which is near the surface of the earth (the lower seven miles, approximately) contains substances given off as impurities by the earth. These can be divided into two classes, molecularly dispersed impurities and those which are present as particles larger in size than average molecules.

Molecular Impurities. Molecularly dispersed impurities differ from the components of the air shown in Table 1.1 in that they are not always present, being restricted to those portions of the atmosphere near the region where they are formed.⁶ How-

⁶ They do not remain permanently in the air in significant amounts for various reasons, e.g., they may be soluble in water, or susceptible to oxidation.

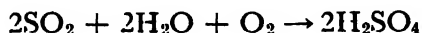
ever, it is difficult to draw a line between such substances and water vapor or carbon dioxide, which are also formed or absorbed at the earth's surface in a highly variable manner.

There are probably dozens or hundreds of gases and vapors produced from time to time in different regions of the earth, but of these, four are perhaps more common than the rest. One is ammonia gas, NH_3 , formed during the decay of plant and animal matter. It is given off from piles of decaying leaves, and from manure, for example. It has a pungent odor, familiar to the reader from his use of household ammonia, a water solution of the gas.

Hydrogen sulfide, H_2S , also given off by decaying plant and animal matter, is another rather common impurity. It has the odor of rotten eggs, or speaking more accurately, rotten eggs have the odor of hydrogen sulfide. The atmosphere around college chemistry laboratories sometimes contains noticeable amounts of this substance.

Another gas found chiefly in civilization centers is carbon monoxide, CO . The formation of this by the burning of coal or of carbon compounds with a deficient supply of air has already been mentioned.

Coal contains small amounts of sulfur compounds, and during combustion the sulfur is oxidized to the gas sulfur dioxide, SO_2 . This colorless substance has a choking odor which is familiar to the reader if he has ever breathed the fumes from hot coal ashes or from burning sulfur. In time, and in the presence of water vapor, sulfur dioxide in the air is oxidized to sulfuric acid, which falls to the earth in very dilute solution in rain.



Dust. Air also contains as impurities particles much larger than ordinary molecules, most of which go under the general heading of dust. This is from many sources. Small dirt particles, lint from cloth, smoke, parts of dead insects, mold, and yeast spores and bacteria are all components of dust. Thousands of particles may be present per cubic foot, and the material is

everywhere, even in the air of a thoroughly cleaned house. Here it is not ordinarily visible of course, but if a strong beam of light is passed through a relatively dark room the particles can be seen at once. Thus, sunlight passing by the edge of a drawn blind, or the beam from a searchlight or a motion picture projector shows the presence of dust very clearly.

Dust is regarded as a nuisance, but actually it performs a useful function. It furnishes nuclei for the condensation of raindrops. When air containing water vapor is cooled, either by expansion or by being mixed with cooler air, the water vapor content of the cooled air may become more than the saturation value. The air is then *supersaturated* with water vapor. This is an unstable, temporary condition which quickly corrects itself by the deposition of liquid water upon any surface in the vicinity. In nature the surface is generally that of dust particles, and the water condenses as rain, clouds, fog, or snow. This explains, in part at least, why rain leaves dirt spots on clean surfaces, such as a freshly washed window or car. These are the dust particles around which the water condensed. If the atmosphere were perfectly clean (and free from ions) the excess water in the air would rapidly condense on the earth's surface, and the objects upon it, as an extraordinarily heavy dew. In a situation like this an umbrella would not be particularly helpful.

Dew and frost are formed in nature, of course, even in the presence of dust particles. But this is because the ground becomes cooler than the air (and its dust particles) as the result of radiation. The water prefers to condense upon the cooler surface. Similar phenomena are familiar in the home, when a kitchen or a bathroom window fogs up as the humidity in these rooms becomes high.

Dust and other small particles in the air also cause many of the optical effects observed in nature, because the blanket of these particles which surrounds the earth permits transmittance of long light waves (red) to a greater extent than short light waves (blue). This explains why sunsets and sunrises are often red. As the sunlight passes through a thicker layer of dust during these

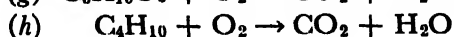
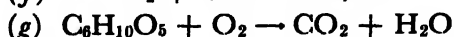
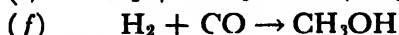
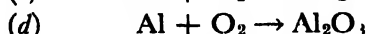
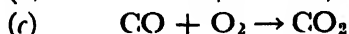
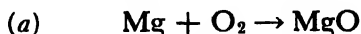
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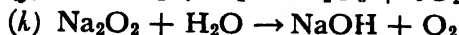
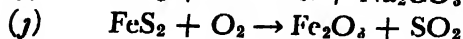
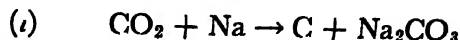
parts of the day more of the non-red components of the light are scattered. The blue color of the sky is due to scattered blue light from the sun which reaches our eyes after it has been turned from its path by dust particles all over the sky. Even at midday the sunlight comes through a layer of this material, hence the sun never appears in its proper color. It is always less red than we observe it. The same light phenomena are seen from artificial light, i.e., the transmitted light is redder and the scattered light bluer than the incident light. For the same reason red light can be seen farther through a fog than light of some other color which contains less of the red component.

Dust is made up mostly of inert particles, but not entirely, since such things as mold, yeast spores, and bacteria are also present. These will grow if they land upon a favorable surface, and everyone is familiar with the formation of mold upon food, the bacterial decay of plant and animal matter, the fermentation of liquids containing sugar (cider to hard cider to cider vinegar, for example) and bacterial infections which may come from the air. Such infections may be checked to some extent by the use of ultra-violet light.

Self Study Questions

1. How does oxygen occur in nature? Give an example of the occurrence of combined oxygen
2. Give two industrial and one laboratory method for preparing oxygen
3. Balance the following





4. Summarize in a sentence the physical properties of oxygen.

5. What is usually meant by the density of a gas? Of a liquid or solid? What is meant by gas density relative to air?

6. If a liter of xenon weighs 5.85 grams and a liter of air weighs 1.29 grams, what is the density of xenon relative to air?

Answer: 4.53.

7. Write five equations illustrating chemical reactions of oxygen.

8. Give the meanings of the terms oxidation, combustion, kindling temperature, spontaneous combustion, exothermic and endothermic reactions. Give examples where possible.

9. If the valence of oxygen is two, zinc two, and chlorine one, what then will be the formulas for zinc oxide and zinc chloride? What will be the valence of tungsten in the compound WO_3 ?

10. Give five uses for oxygen other than those associated with nature.

11. How does ozone differ in its composition and reactivity from oxygen? How is the substance made?

12. What is meant by a reversible reaction? Under what conditions is equilibrium reached in such a reaction?

13. Summarize in a sentence the physical properties of nitrogen.

14. What chemical changes take place in the atmosphere between nitrogen and oxygen in the presence of water vapor and an electric discharge?

15. What is meant by the fixation of nitrogen? How is nitrogen fixed in nature? How by man?

16. How does hydrogen occur in nature? Why would you not expect large quantities of the free element to be present in the atmosphere?

17. Describe industrial and laboratory methods for preparing hydrogen.

18. Summarize in a sentence the physical properties of hydrogen.

19. Write five equations illustrating the chemical behaviour of hydrogen.

20. Define reduction; displacement. Give an example of each process.

21. Hydrogen occurs in traces in the air. Since hydrogen and oxygen form an explosive mixture, why is there not a gigantic explosion whenever the kindling temperature is reached?

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22. Describe at least three methods for preparing carbon dioxide. Include equations, if possible, for the reactions involved.

23. Summarize in a sentence the physical properties of carbon dioxide.

24. Write equations for three reactions illustrating the chemical behaviour of carbon dioxide.

25. What is soda water? Why does it have a slightly sour taste?

26. Explain the formation of limestone caves, and of the deposits often found in these.

27. Describe at least six places in the home where carbon dioxide is either formed, used up, or stored.

28. What is meant by sublimation? Can you give another illustration of this besides the sublimation of dry ice?

29. Name the inert gases in the order of increasing atomic weight. How are these obtained in pure form? Mention several uses.

30. What two types of impurities are found in the air? How do we distinguish between impurities and regular air components?

31. Name four common molecularly dispersed impurities found in air.

32. Name several substances found in dust. What evidence* (optical, biological) do you have that dust is present in a well-cleaned home?

33. What useful function does dust perform in the atmosphere? How does this tie up with present rain-making experiments? How would precipitation take place in the absence of dust or ions?

34. What optical effects in nature are caused by the presence of dust? Explain.

35. What are some of the living components in the air which are associated with dust? What evidence do we have of their presence?

IV

Molecular and Atomic Weights

Early Difficulties in Finding Molecular Weights. So far in the book the masses of individual atoms and molecules have been given in avograms. It is now time to point out that these tiny quantities of matter are not weighable on even the most sensitive

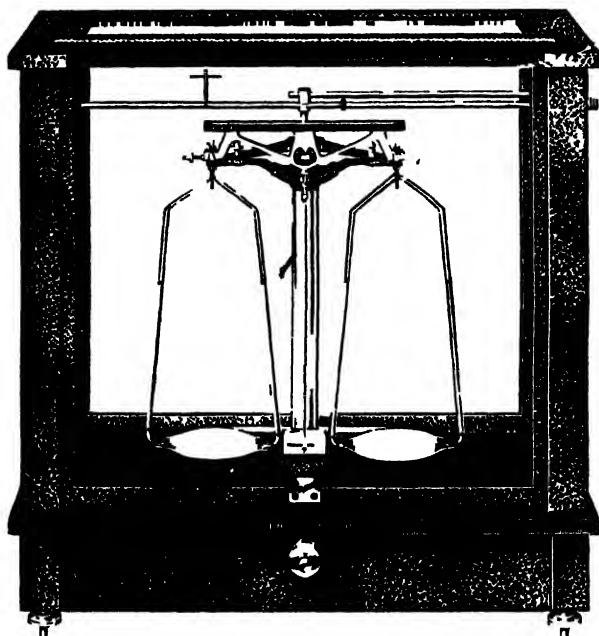


FIGURE 4.1. An Analytical Balance. Courtesy Central Scientific Company.

balance. Weighing in scientific work is commonly done to approximately the nearest 10^{20} avograms, and even the most refined weighing cannot detect less than about 10^{15} avograms. Since an avogram, then, or even many millions of avograms, cannot be

experimentally detected with a balance, it is obviously not possible to determine masses of individual atoms and molecules by direct weighing in the usual sense.¹ In the early history of atomic and molecular weight determinations chemists had not only this



FIGURE 4 2. Analytical Weights Co. rtes, Central Scientific Company.

difficulty to contend with, but in many cases they also did not know the numbers of atoms in different kinds of molecules. The chemists of those days were then forced to do various ingenious things in order to determine atomic and molecular weights.

Avogadro's Law. Avogadro's hypothesis gave them the first opportunity. In the discussion on gas pressure (page 47) it was stated that if the same numbers of molecules of different gases were in similar containers and at the same temperature, they would exert the same pressure. Stated another way, this is the important law (now) of Avogadro: *Equal volumes of all gases under*

¹ However, the masses of individual atoms can now be determined indirectly with the mass spectrograph, described on page 104

the same pressure and temperature contain the same number of molecules. When chemists understood the significance of this law, some fifty years after its proposal as a hypothesis, they realized that by weighing equal volumes of different gases under the same condi-



FIGURE 4.3. Johann Jacob Berzelius (Swedish 1779-1848) The most outstanding chemist of that period. He first used chemical symbols and determined many atomic weights with surprising accuracy, considering the crude facilities of those times.

tions they would be obtaining values which would be in the same ratio as the masses of the individual molecules. Thus, while one oxygen or hydrogen molecule cannot be weighed, it is possible to weigh, say, 10^{22} molecules of each, and these weights will be in the same ratio as those of single molecules. In this way, for example, we can determine that a sulfur dioxide molecule has twice the mass of an oxygen molecule, even though we do not know the mass of either. To make such a method of practical value it was necessary to establish a standard, so that the *relative molecular weights* obtained could be stated in terms of this standard. A relative

molecular weight of 32 for oxygen was chosen as the standard, chiefly because then no atomic weights came out to be less than one. On the basis of this standard, sulfur dioxide had a relative molecular weight of 64. The procedure for determining molecular weights became one of weighing a volume of the gas in question and comparing it to the weight of the same volume of oxygen under the same conditions.

Gram Molecular Weights. Chemists often had occasion to express molecular weights as a definite quantity of matter rather

than as a ratio. Grams were most frequently used, and when this unit was applied to relative molecular weights they became known as *gram molecular weights*. Thus the relative molecular weight of oxygen (32) became 32 grams when expressed as a gram molecular weight. It was found that this weight of oxygen gas had a volume under standard conditions of 22.4 liters, and that the gram molecular weights of other gases under standard conditions also occupied essentially the same volume, as expected from Avogadro's Law. This volume, important to chemists, became known as the *gram molecular volume*.

The method of weighing known gas volumes under known conditions is probably still the chief way in which we determine the molecular weights, or gram molecular weights, of gases. Actually it is not necessary to weigh such a large volume as 22.4 liters (about 6 gallons), nor to have it at standard conditions. A much smaller volume can be weighed at room conditions. The volume can then be corrected to what it would become at standard conditions by applying Boyle's and Charles' Laws; the weight of the corrected volume can then be used to find the weight of 22.4 liters in a direct proportion. This sort of calculation is often carried out with gases, and it is now apparent why problems of the type given in Chapter XXVI are of some importance. The gram molecular weights found by this method are only approximate, because Avogadro's Law is not



FIGURE 4.4. Theodore William Richards (1868-1929). Professor of Chemistry at Harvard University. He received the Nobel prize for his accurate and extensive work on atomic weights.

exact,² and there are not always just 6.023×10^{23} molecules in a gram molecular volume at standard conditions, i.e., real gases do not behave quite like a hypothetical perfect gas.

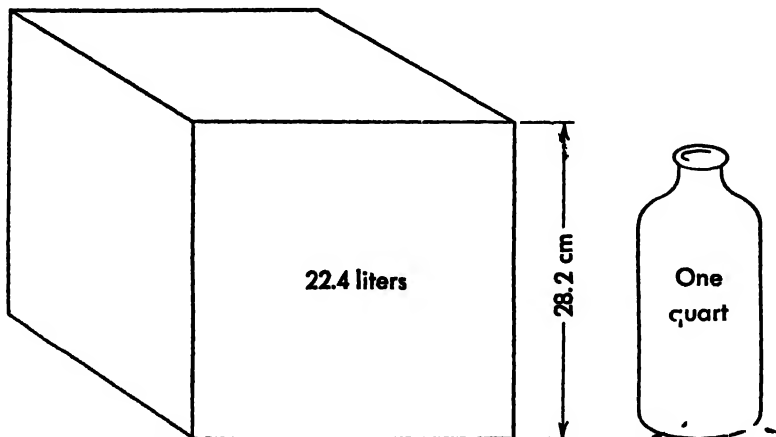


FIGURE 4.5. The Gram Molecular Volume. Its size is here compared to a quart.

The details of determining the accurate molecular weight of a compound lie beyond the scope of this book, but briefly, it is obtained by experimentally determining its formula and then adding up the proper number of accurate atomic weights. Thus, the weight of its vapor might lead to an approximate molecular weight of 80 for the substance benzene. Analysis would show the molecule to contain carbon and hydrogen only, in the atomic ratio of one to one. But the formula might be CH , C_2H_2 , C_3H_3 , etc., since in all of these the ratio is one carbon atom to one hydrogen atom. But one of these gives a molecular weight which is closest to the approximate molecular weight from vapor density. This must be the formula C_6H_6 , since the molecular weight of this molecule is 12.01×6 plus 1.008×6 , or 78.11. This latter value is then the accurate molecular weight.

Relative Atomic Weights. It was next realized that by choosing a type of molecule which contained only one atom of an element, it was possible to determine experimentally the *relative*

² See footnote, page 2.

atomic weight of that element by multiplying the relative molecular weight by the percentage of the element in the compound. Thus, the relative atomic weight of carbon could be obtained by getting experimental data on the gas carbon dioxide. From the relative molecular weight (44) and the percentage of carbon (27.3), the relative atomic weight of carbon then became 44×0.273 , or 12. (As a parallel statement, if a single molecule weighs 44 avograms and contains 27.3 per cent of carbon then the carbon atom must have a mass of 12 avograms.)

The only difficulty with this reasoning was that in the early days of chemistry it was not known whether carbon dioxide ("fixed air") contained one, two, three, or some other number of carbon atoms per molecule, since the atomic weight of carbon was not known, and they had no basis for a formula. While the value of 12 could be obtained as above, there was no assurance that this was not some multiple of the correct atomic weight.

The problem was solved by analyzing a great many gases whose molecules contained carbon atoms, with the thought in mind that if enough were examined one or more would be found whose molecules each contained but one atom of carbon. This is a little like saying that if enough small boys with marbles in their pockets are examined, one will eventually be found with only one marble. No molecule containing carbon has ever been found to have in it less than 12 avograms of carbon (for the common isotope), i.e., the atomic weight of carbon has never been found to be lower than 12. This value is also checked by the position of carbon in the periodic table, and by other, more modern methods.

The grams of an element in 22.4 liters of one of its gaseous compounds whose molecules each contain but one atom of the element has come to be known as the *gram atomic weight*. Thus, the gram atomic weight of oxygen is 16 grams, carbon 12 grams, etc. However, atomic weights found by this method are only approximations, for the same reasons that molecular weights obtained from gas density are only approximations (gases do not behave exactly according to Charles' and Boyle's Laws).

To determine the accurate atomic weight of an element the weight of that element which combines with exactly 8 grams of oxygen or its equivalent in some other element is found by a careful analysis. This quantity, known as the combining weight, gives the accurate atomic weight when multiplied by a small whole number.

Weights of Individual Atoms and Molecules. Shortly after the turn of the century it became possible to determine the actual number of molecules in 22.4 liters of a gas under standard conditions, that is, in a gram molecular weight. The methods for doing this are chiefly of interest to physicists, but there are now several which are independent of each other, and which give values in rather good agreement. The number of molecules in a gram molecular weight and of atoms in a gram atomic weight, 6.023×10^{23} , is known as *Avogadro's Number*. It is thought to have been established to within about 0.02 per cent.

The knowledge of Avogadro's Number has made it possible to calculate the masses of individual atoms and molecules from atomic and molecular weights. These values, in grams, come out to be fantastically small. Thus an atom of hydrogen has a mass of 0.000000000000000000000017 gram. But by using the proper, tiny unit of mass, i.e., the avogram, they can be expressed as quantities numerically equal to the relative and gram atomic and molecular weights.³

The Mass Spectrograph. The most modern method for determining both atomic and molecular weights is by use of the apparatus shown in Figures 4.6 and 4.7, and known, first as the mass spectrograph, and in the modern form in the illustration, the mass spectrometer. When a stream of electrons is passed through a partially evacuated container having in it atoms or molecules whose mass is to be determined, electrons are knock-

³ This explains why the avogram is one gram divided by Avogadro's Number. The mass of one molecule (*A*) of a substance is the gram molecular weight (*B*) divided by this number. For the two masses (*A* and *B*) to be numerically the same (a convenience) the smaller unit (the avogram) must therefore be the larger unit (the gram) divided by 6.023×10^{23} .

out from some of these, causing them to become positive ions. The latter can then be drawn to a negatively charged plate because of electrostatic attraction. If this plate is perforated, some of the positive ions shoot through the opening and out behind. It is these which are studied in the mass spectrometer (Figure 4.7).



FIGURE 4.6 A Mass Spectrometer
Courtesy General Electric Company

A beam of these particles, made narrow by being passed through slits, is bent by a magnetic field. The amount of bending is proportional to the mass of the particles being measured, the light particles being deflected more than the heavy ones. The narrow beam of particles is finally made to hit a collector plate, causing a current which can be amplified to operate a recording pen on graph paper. The particle

beam can also be made to strike a photographic plate, forming a line which appears at its spot when the film is developed. The position of the line on the film (or of the maximum on the recorded curve) shows the mass of the particles which caused it, while the intensity (or height of the maximum) is a measure of the amount of that component. A remarkable accuracy is possible with the instrument, both in the atomic weights of isotopes and in the percentages of isotopes present, as shown, for example, by the results with the element krypton given in Table 4.1.

Mass spectrometers are not necessarily limited to use of magnetic deflection, and much research is going on at the present time in attempts to effect a satisfactory mass separation based upon time of flight of ions from their formation to their arrival at a collector plate.

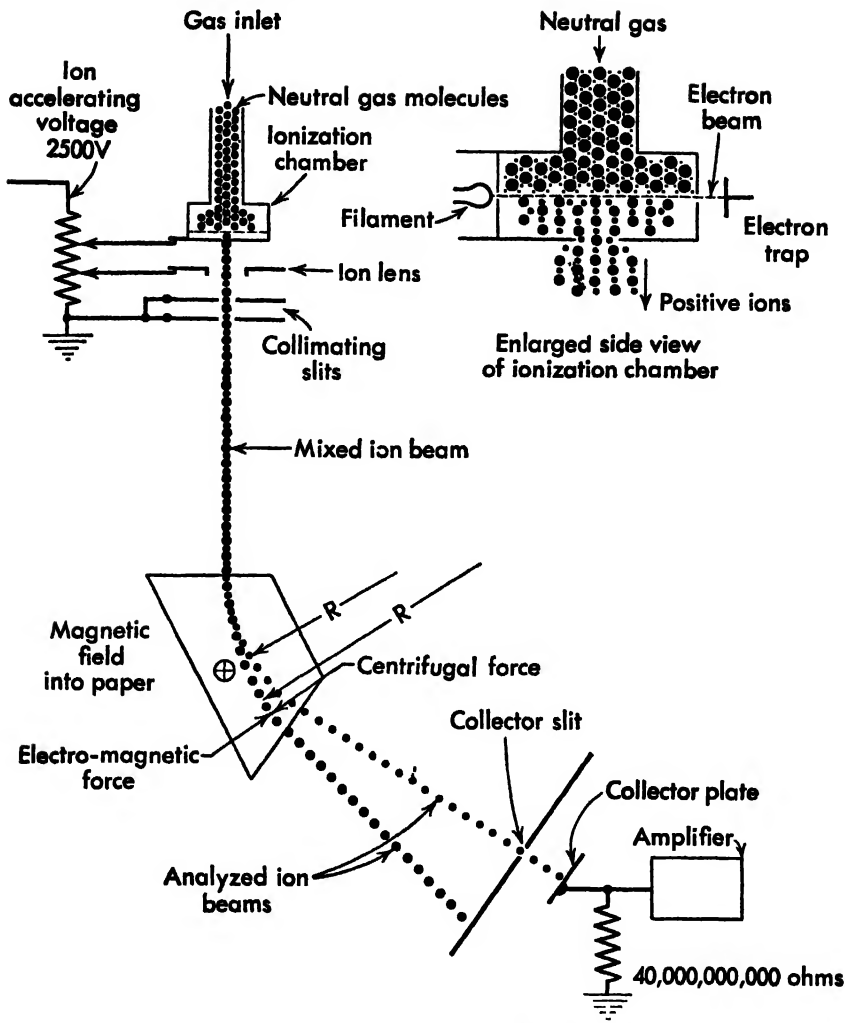


FIGURE 4.7. Diagram Showing Principle of Mass Spectrometer. Courtesy General Electric Company.

TABLE 4.1 **Isotopes of Krypton**

<i>Atomic weight</i>	<i>Abundance</i>
77.926	0.35%
79.926	2.01
81.927	11.53
82.927	11.53
83.928	57.11
85.929	17.47

Summary. The concepts in the section just concluded, difficult for the beginner, can perhaps be made clearer by the following summary. Scientists cannot weigh individual atoms and molecules with a balance, but they do weigh large numbers of them to establish atomic and molecular weights. The mass of Avogadro's Number, or 6.023×10^{23} molecules, is known as the *gram molecular weight* if it is stated in grams. This number of molecules makes up close to 22.4 liters of all gases at standard conditions. The weight in grams of Avogadro's Number of atoms is known as the *gram atomic weight*.

The same numbers, without units, are known as *relative atomic and molecular weights*, or simply as atomic and molecular weights. These numbers are ratios based upon a standard value of exactly 16 for the atomic weight of oxygen and 32 for its molecular weight.

The types of atomic and molecular weights which have been described can be illustrated by considering atoms and molecules of iodine, as shown in Table 4.2.

TABLE 4.2. Atomic and Molecular Weights of Iodine

Mass of one atom of iodine	= 126.92 avograms
Gram atomic weight of iodine (mass of 6.023×10^{23} atoms)	= 126.92 grams
Relative atomic weight of iodine	= 126.92
Mass of one molecule of iodine (I_2)	= 253.84 avograms
Gram molecular weight of iodine (mass of 6.023×10^{23} molecules)	= 253.84 grams
Relative molecular weight of iodine	= 253.84

Relative atomic and molecular weights are much more widely used than any others in chemical conversation and writing, not because they are easier to understand, or convey a special meaning, but simply because it is easier and quicker to use these numbers without attaching a unit.

Methods have been described here for finding atomic and molecular weights based upon the experimental study of gases. There are also a number of other methods available for determining atomic and molecular weights which apply to gases, liquids,

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or solids. The mass spectrograph and mass spectrometer are the most modern instruments for determining atomic and molecular weights.

A number of important calculations involving atomic and molecular weights are given in Chapter XXVI.

Self Study Questions

1. State Avogadro's Law. Explain how this serves as a basis for determining the relative molecular weights of gases.
2. How is the relative atomic weight of an element which forms many gaseous compounds determined?
3. State three kinds of atomic weights for the element phosphorus, and give the significance of each.
4. State three kinds of molecular weights for hydrogen sulfide₂ and give the significance of each.
5. Calculate the molecular weight of table sugar, $C_{12}H_{22}O_{11}$, from the atomic weights of its constituent elements.
6. Describe briefly the operation of the mass spectrograph.
7. What is the weight of a liter of propylene gas (C_3H_6) at standard conditions?

PART TWO

Water and Its Inorganic Solutes; Solutions

V

Water; Ice

PHYSICAL BEHAVIOUR OF WATER

The Change from Water Vapor to Liquid Water. When water vapor is cooled, a temperature is eventually reached at which its molecules condense together at a faster rate than they fly apart, and liquid water results. The temperature at which this

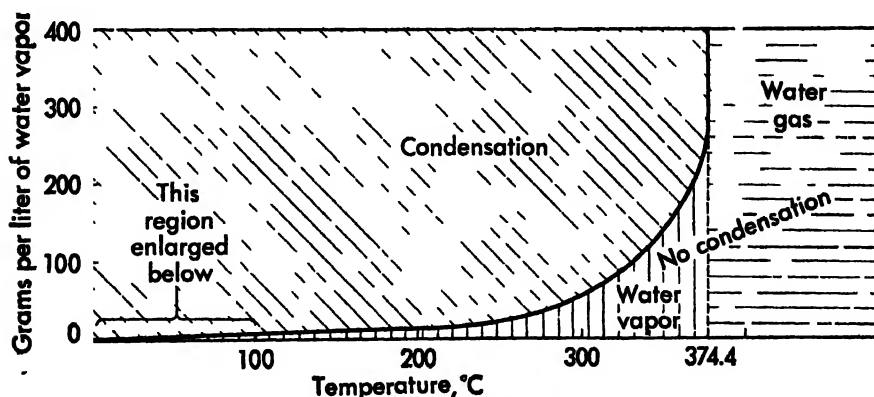


FIGURE 5.1. Condensation of Water Vapor Concentrations necessary for condensation from the freezing point to the critical temperature.

transformation takes place depends upon the water vapor pressure, and hence upon the concentration of the water vapor in space, as shown by the graph in Figure 5.1. This gives the complete range of condensation temperatures, from the critical temperature down to the freezing point. The reader is perhaps more interested in the portion of the same curve from 0°C. to 100°C., shown in Figure 5.2. Thus a liter of steam at 100°C. contains about 0.6 gram of water vapor at saturation, and if

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this is cooled to, say, 50°C ., about 0.5 gram of this will condense to liquid water and about 0.1 gram will remain in the saturated vapor at the lower temperature.

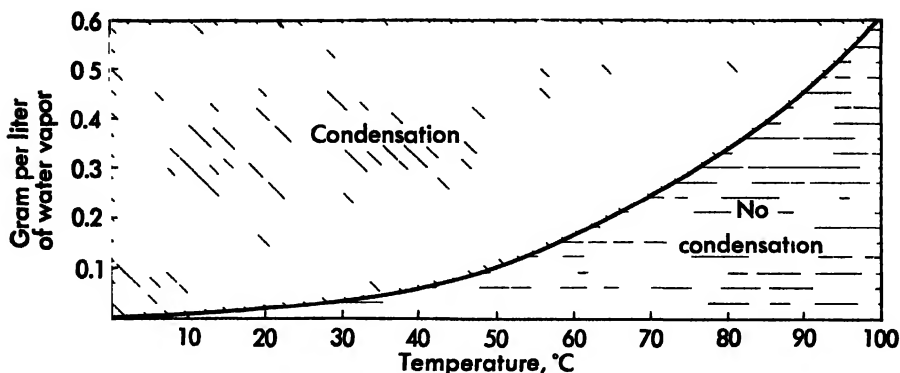


FIGURE 5.2 Enlargement of the Curve in Figure 3.1 to show the Region between 0°C and 100°C

The change from water vapor to liquid water is a common phenomenon in nature. It occurs when water vapor is cooled to a point where its concentration permits the liquid to form, as when moist, warm air in the house comes in contact with a cool window, or when dew deposits upon objects which have cooled by radiation. Fog and cloud formation is another example of this change.

The conversion of water vapor to liquid water, or stated more generally, of any vapor to the corresponding liquid, is known as *condensation*. The process is reversible, and the opposite change, from liquid water to water vapor (evaporation) and from ice or snow to water vapor (sublimation) also frequently occurs. In a closed container partly filled with water or ice at constant temperature condensation and evaporation (or sublimation) go on at the same rate, causing a state of dynamic equilibrium to be reached (Figure 5.3). But in nature one of the two processes generally takes place more rapidly than the other at any given time.

Molecular Motion in Water. The molecules in water and other liquids, like gas molecules, are in continual translational,

rotational, and vibrational motion, even in a specimen of liquid which appears perfectly quiet to the human eye. This motion can be demonstrated by examining in water an object which is so small that high magnification is required to see it. The object is observed to move around in a random manner as if colliding with invisible particles (the Brownian Movement, page 46), evidence almost as direct as if we could see the moving molecules themselves. Calculations indicate that an object one micron in diameter will be run into in this manner about 10^{20} times each second when it is suspended in water at ordinary temperatures.

Density of Water. The density of water in grams per milliliter at various temperatures is given in Table 5.1. The increase in density from high temperatures down to 4° is what one would expect, because as the temperature drops the various molecular movements diminish and permit closer packing. But from 4° to the freezing point water is a unique liquid, since its density *decreases* with falling temperature. Ice is also an unusual solid since it is considerably less dense than water, whereas most liquids form denser solids when they freeze. A thermometer containing water would be a puzzling instrument between 4° and zero, because as the temperature dropped the liquid level would rise, and at 1° , for example, the reading would be the same as at 7° . The reason for this odd change in density is given later (page 116).

The change in density of water with temperature accounts for the behaviour of a quiet body of water as it cools in the fall of

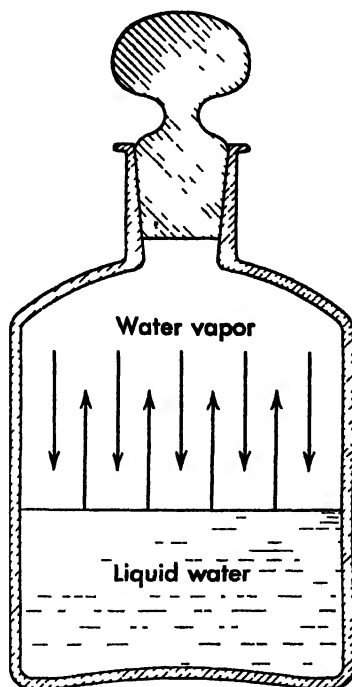


FIGURE 5.3 Condensation and Evaporation. Equilibrium exists in a closed container at constant temperature, since both processes go on at the same rate

TABLE 5.1 Variation of Density of Water with Temperature

<i>Temperature</i>	<i>Density</i>
250°C.	0.794 g. 'ml.
100°	0.958
50°	0.988
25°	0.997
10°	0.9997
7°	0.99993
4°	1.00000
3°	0.99999
2°	0.99997
1°	0.99993
0°	{ 0.99987 (water) 0.917 (ice)

the year. As the temperature of the surface is lowered by the air this portion sinks, to be replaced by the less dense, warmer, underlying water. The up and down movement continues until the entire body of water has cooled to 4°C., after which the surface water cools further without sinking, because its density is now diminishing as the temperature falls from 4°C. When the surface water reaches the freezing point ice then forms from the top down. This has an important bearing upon conditions in the colder regions of the earth. If ice followed the general tendency of solids to be more dense than the liquids from which they form, bodies of water would freeze from the bottom up. In cold regions melting would take place during the summer months only at the surface, discouraging marine life and shipping.

Other Physical Properties of Water. Many of the physical properties of water listed in Table 5.2 are familiar to the reader. The specific heat, or calories of heat necessary to raise one gram of a substance one degree Centigrade, is unusually high in the case of water, i.e., one calorie of heat raises the temperature of a gram of most substances far more than one degree. A gram of alcohol, for example, will become nearly two degrees hotter when it absorbs a calorie of heat, and a gram of copper about eleven degrees. The high heat capacity of water has important consequences. Consider, for example, how much less would be

TABLE 5.2 Physical Properties of Water

COLOR	Colorless, but bluish in thick layers.
ODOR	None.
TASTE	Non perceptible. However, unpleasant in absence of dissolved air.
BOILING POINT	100°C. at 760 mm. pressure.
FREEZING POINT	0°C. at 760 mm. pressure, but much higher under large pressures.
CRITICAL TEMPERATURE	374.4°C.
CRITICAL PRESSURE	217.72 atmospheres.
SPECIFIC HEAT	Approximately one. Exactly 1.0000 between 15° and 16°C.
DENSITY	1.00000 g./ml (water at 4°C.).

the influence of the oceans upon our climate if the specific heat of water were but a fractional amount of its true value. Note also what would happen to the temperature of the human body, largely water, after violent exercise!

The boiling and freezing temperatures, specific heat, and density of water happen to have such values as 100, zero, and one because water was the standard substance used in establishing these scales.

CHEMICAL PROPERTIES OF WATER

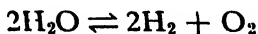
Association. The structure of the water molecule has already been described (page 39), and water vapor consists of these individual units. But in liquid water there is an attraction between molecules because of their polar nature.¹ As a result,

¹ The water molecule is V-shaped, the angle of the V being 105°. Furthermore, the shared electrons between hydrogen and oxygen actually spend most of their time in the part of the molecular orbital belonging to oxygen. This causes the oxygen part of the molecule to be more negative than the hydrogen part, and a polar molecule is the result, i.e., one in which the center of the negative charge does not coincide with the center of the positive charge. The polar nature of the water molecule is sometimes indicated by using the figure $\oplus\ominus$. Molecules of this type tend to associate because of the attraction between the oppositely charged parts, e.g., $\oplus\ominus \oplus\ominus \oplus\ominus$. In this association a hydrogen atom of one water

aggregates of H_2O molecules form which are loosely held together, and which are continually breaking up and reassembling. When molecules form aggregates in this manner, *association* is said to take place.

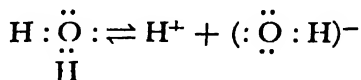
With lowering of temperature the aggregates become larger, and more stable. These apparently cannot fit together as closely as the smaller aggregates, and we account for the steady decrease in the density of water from $4^\circ\text{C}.$ to the freezing point by the tendency of water molecules to spread out as these aggregates increase in size. The usual increase of density of liquids with falling temperature, produced by the closer packing of molecules as molecular and atomic movements diminish, is therefore reversed in the case of water from $4^\circ\text{C}.$ to the freezing point.

Thermal Decomposition of Water. Water breaks up at very high temperatures into its constituent elements in a reversible manner.



The extent of the decomposition increases with the temperature. At $2700^\circ\text{C}.$ about eleven per cent of the molecules in a sample will be broken up into the elements hydrogen and oxygen.

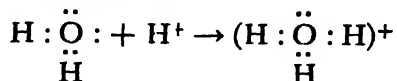
Ionization of Water. At ordinary temperatures water molecules dissociate, to a very slight extent, in another way. Charged, part-molecules are formed, known as hydrogen ions and hydroxide ions.



Only about one water molecule in half a billion is ionized at any given time, at room temperature. Actually these ions are hy-

molecule is drawn to the oxygen atom of another, causing the two molecules to be held together by what is known as a hydrogen bond. The V-shape of the water molecule is hence of great significance in determining the properties of water, since a molecule with the linear structure $\text{H} : \underset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \text{H}$ would not be polar and would not associate. This would cause it to have a lower freezing and boiling point. If water molecules had this linear structure water would in all probability be a gas at ordinary temperatures.

drated, i.e., they have water molecules attracted to them. Thus, in the case of the hydrogen ion:



The H_3O^+ ion is known as the *hydronium* ion.

Reactions of Water with Other Substances. Water reacts with oxides of active metals to form substances known as *bases*. Thus, sodium oxide yields the base sodium hydroxide with water.

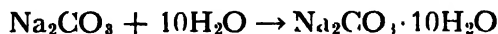


Nonmetallic oxides combine with water to form *acids*. As an example, nitrogen pentoxide, N_2O_5 , gives nitric acid.



Acids in water solution taste sour and turn blue litmus paper red, while bases in water solution feel slippery, taste bitter, and turn red litmus paper blue. These substances exist in ionized form in water, although this is not shown in the two equations just written. Ionization and ionic equations will be discussed in Chapter VII.

Water also combines with many substances, most of which are salts, to form *hydrates*. These are compounds in which water molecules make up part of a crystal structure, and usually exert an appreciable vapor pressure. For example, when sodium carbonate is crystallized from water solution it comes out with ten molecules of water in its crystals (washing soda)



The use of the dot in the formula $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ should be explained. In hydrates the hydrogen and oxygen atoms of water are not bound as firmly to the remaining substances as are the atoms in most molecules. They tend to remain combined with each other as water, as shown by the fact that most hydrate crystals exhibit a significant water vapor pressure. The tendency to remain as water molecules in the crystal and the loose combination of these with the rest of the crystal (usually with the

metal ions) is shown by using a dot between the water of hydration and the rest of the compound.

If the vapor pressure which the hydrate water exerts is greater than the water vapor pressure of the air, water molecules

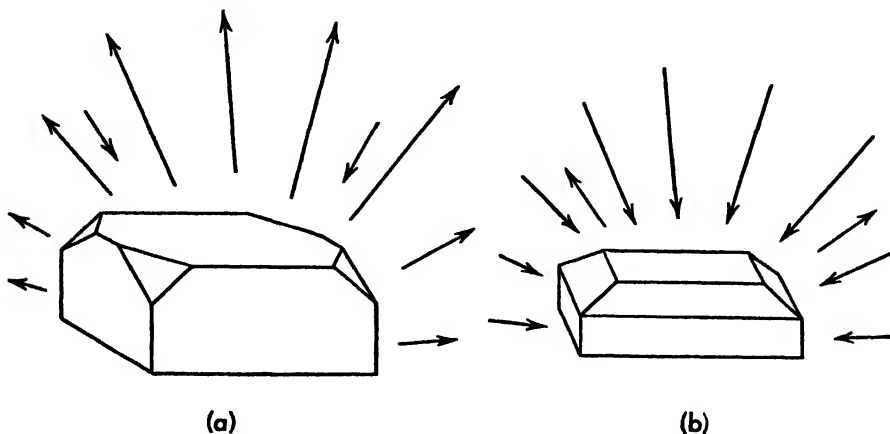


FIGURE 5.4. Efflorescence and Deliquescence. Hydrate crystal (a), losing water faster than it gains it from the atmosphere, will eventually crumble to a powder (efflorescence). Crystal (b), gaining water from the atmosphere more rapidly than it gives it off, will become moist, and may even dissolve in the water it collects (deliquescence).

leave the hydrate crystals and the latter crumble away to a powder. This phenomenon is called *efflorescence*. On the other hand, hydrates and other compounds sometimes attract water to their surfaces in such quantities that they become moist, or even dissolve in the water to form a solution. This behaviour is known as *deliquescence*. It is observed particularly with very soluble salts, such as calcium chloride, whose saturated solutions exert a relatively low vapor pressure.

Acids, bases, salts, and hydrates will be more clearly understood after study of electrolytes and ionization in Chapters VI and VII.

NATURAL WATERS

Natural Waters Not Pure. The section just completed deals with pure water. But the vast amount of this fluid which covers nearly three quarters of the earth's surface is not pure, even

that which comes from melting snow and ice. This general lack of purity is partly due to the presence of suspended impurities, such as fine clay particles and microorganisms, and partly due to the fact that water is such an excellent solvent, one of the best among the many known liquids. Everyone is familiar with the solvent action of water in the case of highly soluble substances such as salt or sugar, but water also exerts a lesser dissolving action upon sparingly soluble materials, such as air, glass, or various minerals.

Types of Impurities in Natural Water. Impurities in natural water can be divided into two groups based upon particle size. In the one group are such things as dirt, microorganisms, and in general objects larger in size than ordinary molecules. In the other group are the molecular and ionic impurities.

Dissolved air is a common molecular impurity in natural water. The solubilities of the two major components of the air are not the same, as shown by the data below.

Percentage of nitrogen in air	78
Percentage of nitrogen in air recovered from water . .	67
Percentage of oxygen in air	21
Percentage of oxygen in air recovered from water . .	33

The dissolved oxygen in water is of great importance to fish, since they use it, like land animals, to oxidize ingested food. They have special organs (gills) for removing oxygen from water.

Natural waters also practically always contain dissolved salts. Sodium chloride is the commonest of these, but also very prevalent are chlorides, bicarbonates, and sulfates of calcium and magnesium. If these salts are such that they interfere with the normal action of soap the water is called hard. Hard water will be discussed in greater detail in the chapter on cleaning agents (Chapter XXIV). Some causes for colors and precipitates in natural water are given in Appendix D.

Treatment of Natural Water for Use in Population Centers. The water supply of cities and towns must be free from sediment

and pathogenic microorganisms, and the large scale treatment of natural water to accomplish this is therefore an important municipal function. A number of methods are in use, including

(a) mixing of water with a small amount of aluminum sulfate and allowing it to stand in large settling basins. The aluminum sulfate hydrolyzes (page 160) to aluminum hydroxide, a flocculent precipitate, which carries impurities down with it as it settles; (b) filtration of the water through sand; (c) treatment of the filtered water with a small amount of chlorine, to destroy microorganisms. As little as one part per million of chlorine kills most harmful bacteria.

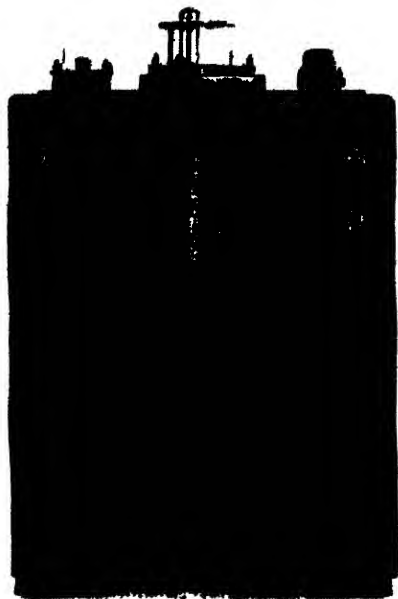


FIGURE 5.5. Chlorinator for Public Water Supplies. Chlorine gas, supplied in tanks under high pressure, is reduced to a near vacuum in the glass bell jar. From here, the gas is drawn through a metering orifice to an injector where it is thoroughly mixed with a small stream of water. This chlorine solution is then fed to the main water supply. Courtesy Wallace & Tiernan Company, Inc.

ICE

When water cools to 0°C . (32°F .) it goes through the familiar change to ice. This process is a continuation of the tendency, exhibited by water molecules above the freezing point, to associate together in groups. At 0°C . the aggregating force overcomes the random

movements of molecules from place to place and causes them to become fixed in position. Thereafter molecular motion still takes place, but it becomes vibrational in character.

The whole body of water does not suddenly become ice as the temperature reaches 0°C . Ice crystals need favorable surfaces upon which to form and grow—preferably other ice crystals, or at least solids with a similar structure.

In the absence of such a surface the water may cool considerably below 0°C . (undercooling²). This unstable condition is overcome by the presence of the proper surface, even though in minute amount, such as a tiny ice crystal, a speck of dust, or a scratch in the container. When ice crystals begin to form in undercooled water they grow rapidly, and the temperature quickly rises to the freezing point, because of the heat given off by water as it changes to ice (79 calories per gram are emitted as water at 0°C . changes to ice at 0°C .).

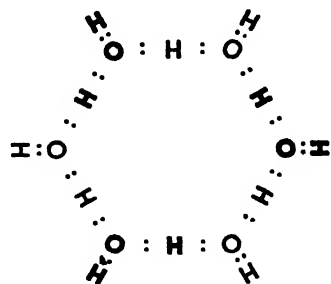


FIGURE 5.6. A Unit in the Structure of Ice.

During formation of ice the faces, edges, and corners of the crystals can be clearly seen, but after freezing is complete the ice is likely to appear glasslike rather than crystalline. In all forms of frozen water in nature (ice, snow, frost, hail, rime, etc.), the individual water molecules make groups of hexagons like the one shown in Figure 5.6. In this drawing each oxygen atom has only six electrons around it. The other two, not shown, are shared with the hydrogen atoms of other water molecules above or below the plane of the paper to make a three-dimensional structure.³ When ice is able to form freely in space this hexagonal unit influences the shape of the resulting crystal. It is thus we account for the shape of snowflakes, and the reader can visualize, on a vastly expanded scale, how the latter grow, in terms of the structure of ice, somewhat as indicated by the drawing in Figure 5.7.

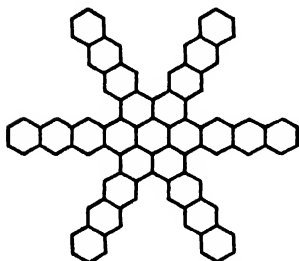


FIGURE 5.7. Basic Manner in Which a Snowflake Gets Its Shape.

² Very clean water has been undercooled to -39°C . Undercooling sometimes takes place in clouds, which then contain water droplets below the freezing point. Silver iodide, with a crystal structure somewhat like ice, is used to start ice formation, and hence precipitation, in such clouds.

³ It is now believed¹, however, that hydrogen atoms can share but one pair of electrons. In the hydrogen bond, therefore, part of the bonding must be due to electrostatic attraction between polar molecules.

When ice crystals form the space between molecules becomes greater than the average distance separating molecules in liquid water. The density of ice (0.917) is hence less than that of water, and ice floats on water about ten elevenths submerged. When one views an iceberg he must mentally multiply the visible bulk by eleven, therefore, to gain a true picture of the entire object. Other kinds of ice have been formed, by cooling water under pressure. Ices II, III, V, VI, and VII, all different from ordinary ice, ice I, have been made. Ice VI, for example, made at 6500 atmospheres pressure, has a density of 1.09 and may melt at a temperature as high as 50°C. Some of these forms exist in nature.

Self Study Questions

1. A liter of saturated water vapor at 80°C. is cooled to 30°C. From the graph in Figure 5.2 calculate approximately how much liquid water will form by condensation.

2. A liter of water vapor, not saturated, contains 0.1 gram of the vapor at 55°C. If the volume is diminished to 500 ml. without changing the temperature, will liquid water condense out, and if so, how much?

3. Give several examples in nature in which liquid water forms from water vapor and give the reason in each case.

4. What word is used to describe the situation in which two opposing processes go on at the same rate? Under what conditions will this situation occur in the case of condensation and evaporation of water?

5. What evidence do we have that molecular motion is taking place in an apparently quiet specimen of water?

6. How does the density of water vary as the temperature diminishes from 10° to zero? What movements will take place within a body of fresh water as it cools over this temperature range?

7. How are individual H₂O molecules thought to be held together in the aggregates which characterize liquid water? How do we explain the decrease in density of water below 4°C.? How would a water thermometer behave between 10°C. and 0°C.?

8. What is meant by the term "specific heat?" How does the specific heat of water compare with that of most other substances? Does this have any important bearing upon our lives?

9. Write an equation showing how water decomposes at high temperatures. Is this a reversible change? Would you expect the pressure of a sample of very hot steam to be greater or less as the result of this decomposition?

10. Write an equation showing how water molecules dissociate into ions. Is the percentage of liquid water molecules which break up in this manner at ordinary temperatures large?

11. Show by the electron dot convention how such ions can take on water molecules and become hydrated. What is the hydronium ion?

12. Give examples of reactions between water and other substances to form (a) acids, (b) bases, (c) hydrates. What is meant by the terms "efflorescence" and "deliquescence"? Explain these phenomena in terms of water vapor pressure.

13. Give examples of (a) impurities present in natural water with particle sizes larger than molecular, (b) impurities which are molecularly or ionically dispersed.

14. How is water treated for use in large population centers?

15. What is the characteristic arrangement of H_2O molecules in ice and other forms of frozen water found in nature? How are these molecules believed to be held together?

16. What is undercooling? Explain how it can be made to occur, and how it is avoided, in the change from water to ice.

17. Are different forms of ice possible besides that found in nature? How are they made? How many milliliters will a pound of ice I occupy? A pound of ice VI? (Table 5.1, also Appendix H.)

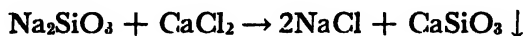
Answer: 495 ml.; 416 ml.

VI

Salt and Its Constituent Elements

The following discussion deals chiefly with the familiar substance table salt. However, it will be shown later that the term "salt" also applies to a whole group of chemical compounds with certain characteristic properties in common. Table salt (sodium chloride) is merely the best known of these.

Occurrence of Salt. We do not know how salt originally formed on the earth. Possibly as the latter cooled by radiation from what we believe was originally a very hot state the chlorine atoms present combined with the most plentiful metal atoms (aluminum, iron, calcium, etc.) to form salts which for the most part were not sodium chloride. At the same time a vast amount of water was forming and condensing; eventually these chlorides would have found their way into solution. Here they would undoubtedly have reacted with such soluble sodium salts as the silicate or carbonate, forming precipitates and leaving sodium chloride in solution. For example, calcium chloride and sodium silicate would react:



During this period of the earth's history, therefore, sodium chloride may well have occurred almost entirely in dissolved form in the oceans.

With passage of geological time some of these bodies of water became landlocked in arid regions and evaporated. This resulted in the deposition of salts, the chief one being sodium chloride. Indeed, the same process goes on today in the Great

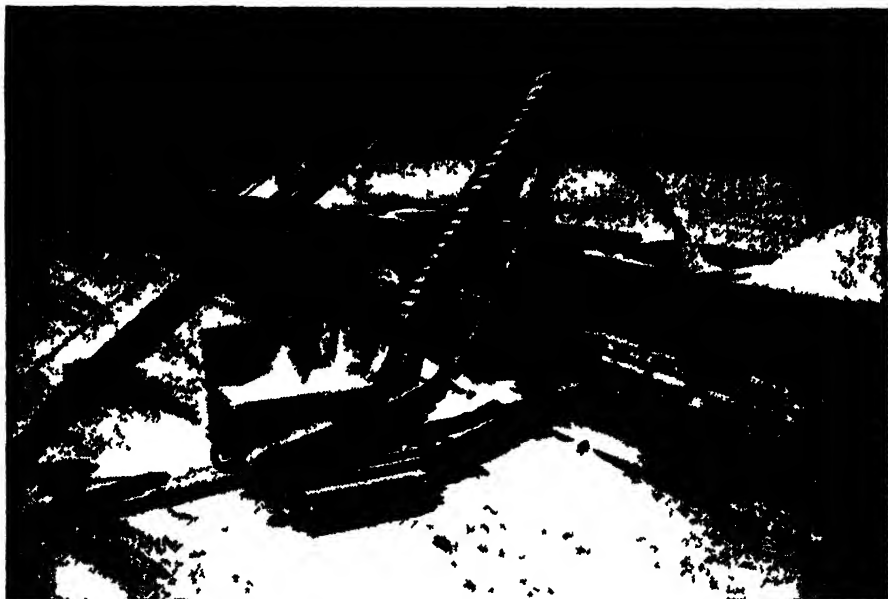


FIGURE 6.1. Coarse Salt is Made by Solar Evaporation at Saltair, Utah. Courtesy Morton Salt Company.

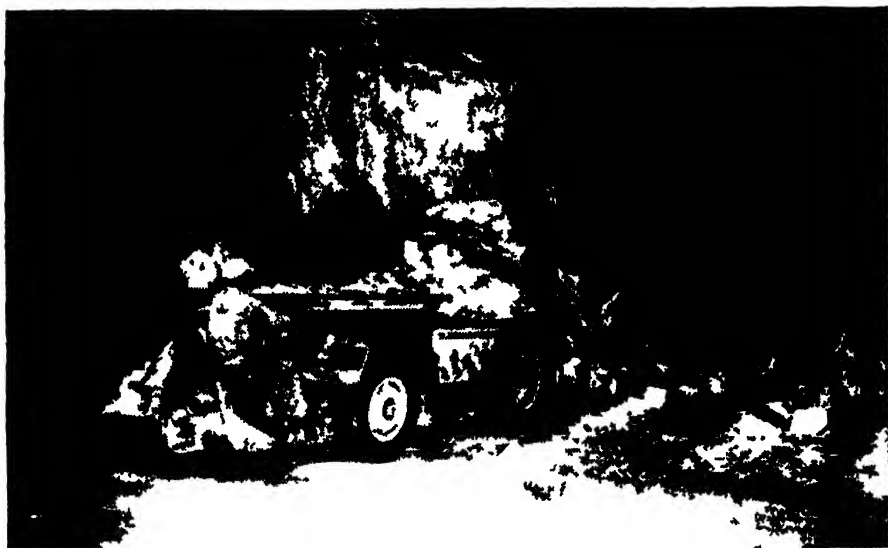


FIGURE 6.2. Mining Salt at Grand Saline, Texas. The loader (right center) drags in newly blasted salt to a conveyor which puts it on the shuttle car shown for transportation to another conveyor or a mine train. Courtesy Morton Salt Company.



FIGURE 6.3. Vacuum Evaporators. Table salt, made up of small crystals like those magnified in Figure 6.7, is obtained in this type of evaporator. Courtesy Morton Salt Company.

Salt Lake and Dead Sea regions. When salt water from the ocean evaporates its salts come out in the order of solubility, first appearing the sparingly soluble ones like calcium sulfate, then the major component sodium chloride, and finally the more soluble and scarcer salts of magnesium and potassium. This has happened frequently in nature, sometimes on a large scale, as for example in central Europe. The evidence shows us that in some regions evaporation, reflooding, reevaporation, etc., took place many times, and caused the formation of complicated salt beds which are hundreds and sometimes thousands of feet thick. Salt domes have also been found in which underground evaporation apparently took place, producing a constantly increasing quantity of solid salt which appears to have pushed up the overlying rock strata.

The chief sources of salt today are from deposits laid down by past evaporation of sea water. In this country extensive beds are found in Texas, Utah, New York, Michigan, California,

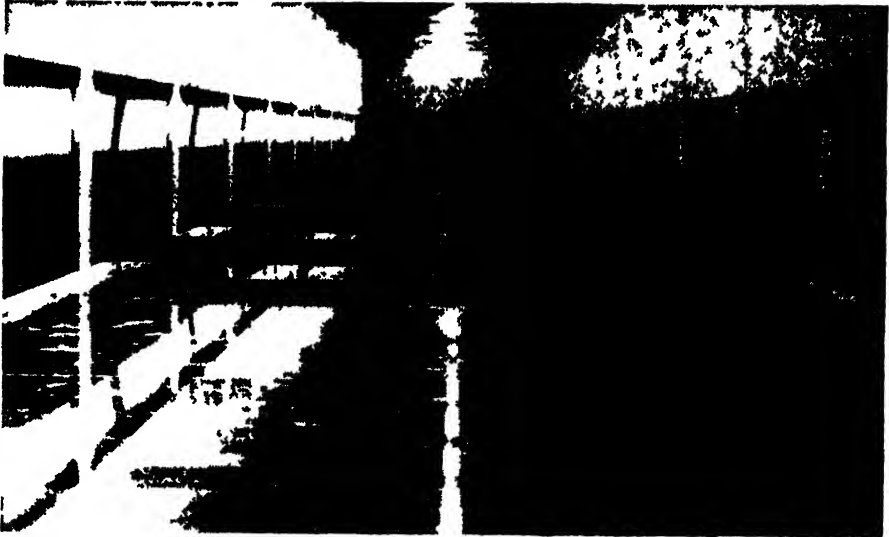


FIGURE 6.4 Open Evaporator Salt obtained by evaporation of brine in this manner is made up of flat, flaky crystals Courtesy Morton Salt Company

West Virginia, and Ohio. Probably the best-known foreign deposit is at Stassfurt, in what is now the Russian zone of Germany. The ocean is still used to a minor extent as a source of salt, particularly in regions where much sunshine and lack of rain makes solar evaporation practicable. In this country salt is so obtained in Utah, from Great Salt Lake (Figure 6.1). The salt content of the oceans is tremendous, being more than a dozen times the entire land mass of the continent of Europe above high water mark, according to one calculation.

Salt Mining. Most salt is obtained from underground deposits which may either be mined in solid form, like coal, or reached with water pipes from the surface and brought up as a saturated brine. An example of the first method is the Texas mine shown in Figure 6.2. The second method is used in Michigan (Figure 6.3). Here the salt is either recovered by a vacuum evaporation which yields the small crystals familiar in table salt, or from open evaporators (Figure 6.4) which yield coarser crystals used in bread, cheese, butter, and the dry salting of meat.

Structure of Salt. Sodium chloride, NaCl , has one atom of the element sodium for each chlorine atom present. But the atoms of these two elements are not joined together by shared electrons as are the substances found in the atmosphere. Consider the

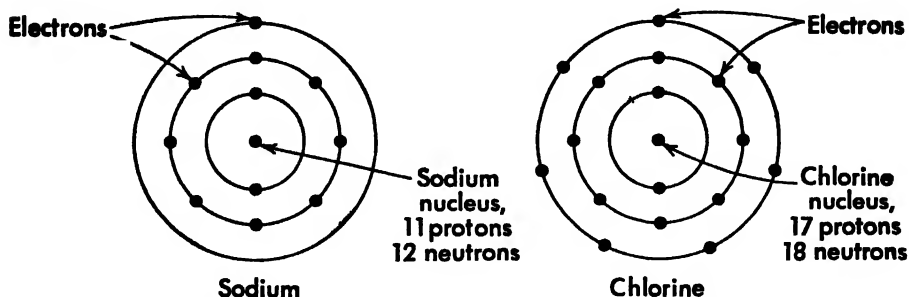


FIGURE 6.5. Atomic Structures of Sodium and Chlorine.

atomic structures of the common isotopes of the elements sodium and chlorine, given in Figure 6.5. Each has three shells of electrons. If these atoms were held together in common salt by shared electrons according to the rule of eight they would have to share eight electrons by a peculiar arrangement in which one of the eight was furnished by sodium and the other seven by chlorine. But salt has properties which are very different from what we would expect if its atoms were joined together by eight shared electrons. The evidence indicates that instead of such a bonding the chlorine atom draws the single outermost sodium electron to itself. This captured electron then becomes part of the outer shell of electrons around chlorine, and the total number of electrons in that shell becomes eight.

Observe the results of this transfer (Figure 6.6). The sodium atom has lost its single outer electron, it has decreased in size, and what was previously the second shell of electrons from the surface now becomes the outer shell. It consists of eight electrons, the stable number. Chlorine also has eight electrons in its outer shell—the original number of seven plus the one acquired from sodium. The resulting electron configurations now satisfy the rule of eight, but without the sharing of electrons. It is these units, different in size, charge, and properties from neutral sodium and

chlorine atoms, which make up salt. The question then arises, how are the atoms held together, if not by shared electrons?

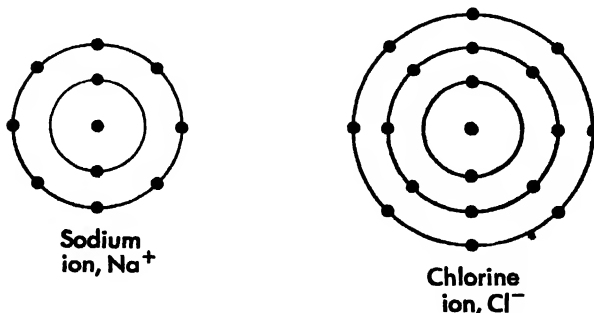


FIGURE 6.6. Atomic Structures of Sodium Ion and Chloride Ion.

Binding Force in Salt. The attraction between atoms which holds them together in salt is thought to be the electrostatic force which causes oppositely charged particles to adhere to each other, as for example when one's hair is attracted to a comb in cold, dry weather. With the transfer of electrons from sodium atoms to chlorine atoms each becomes oppositely charged, as can readily be seen by considering the number of electrons and protons. Each sodium atom (11 protons, 10 electrons) now has one positive charge and each chlorine atom (17 protons, 18 electrons) one negative charge. As mentioned earlier (page 31) these charged atoms are known as *ions*, and the ionic condition is shown by writing the symbols with the proper number of charges, e.g., Na^+ , Cl^- . Electrostatic attraction, therefore, is the binding force which holds the salt ions together.

Salt is, then, a solid made up of ions. The latter remain in fixed positions, but vibrate around these positions in thermal movements which increase in violence with temperature up to 804°C . At that point thermal vibrations become so great that the electrostatic attraction between the ions is no longer strong enough to hold them in place and the salt melts to a liquid in which the ions move in a random manner throughout. The liquid in turn vaporizes at 1413°C .

Electrovalent Compounds; Electrovalence. Substances made up of ions in this way are called *electrovalent*, in contrast with *covalent*

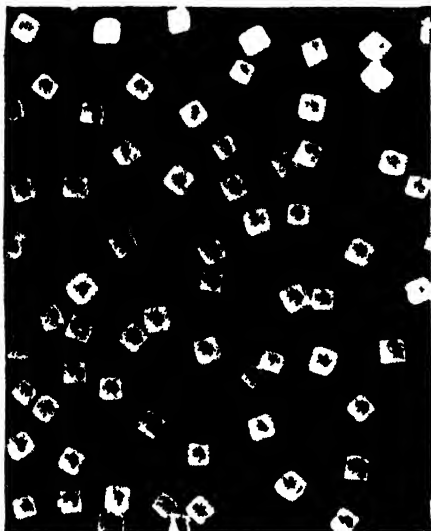


FIGURE 6.7. Salt Crystals. Courtesy Morton Salt Company.

compounds formed when electrons are shared (as in the case of carbon dioxide, for example). There are many electrovalent substances, but when one considers all chemical compounds, the covalent molecules are considerably in the majority. Electrovalent substances, particularly those which are water soluble, are known as *electrolytes*, because their aqueous solutions conduct electricity. They are divided into the three classes *acids*, *bases*, and *salts*, and these will be discussed in the next chapter.

The charge on the ions of an element resulting from loss or gain of electrons in the manner just described is known as the *electrovalence* of that element. When sodium is in the form of sodium ions, Na^+ , it is exhibiting an electrovalence of plus one, for example, while in the case of the chloride ion, Cl^- , the electrovalence is minus one. The electrovalences of some important ions are given in the table on page 162.

Crystals. Solid salt is crystalline, which means its constituent ions are arranged symmetrically in space. The pattern in salt is

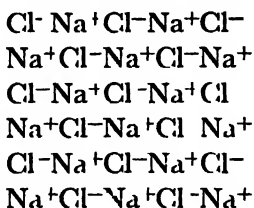


FIGURE 6.8. Cross Section Through a Tiny Salt Crystal.

one of alternating sodium and chloride ions as shown above in the cross section through a very tiny crystal.

In a three-dimensional crystal each interior sodium ion is surrounded by six ions of chlorine, and each ion of chlorine by six sodium ions.

The characteristic arrangement of ions, atoms, or molecules in a crystal determines its habit, i.e., its shape, and the angles which its faces make with each other. In the common form of sodium chloride the angles between the faces are all 90°. Such crystals are called cubic when their sides are equal in length, tetragonal or rhombic when they are not. Salt crystals form cubes. Other types of faces may develop upon occasion, however, such as those shown in Figure 6.9.

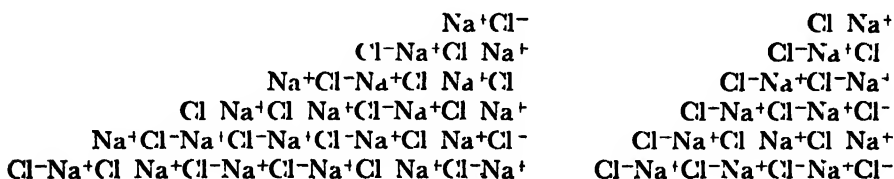


FIGURE 6.9. Other, Less Common Crystal Faces of Salt.

Other Physical Properties of Salt. Sodium chloride has other physical properties of interest. It is able to transmit infrared (heat) radiation much better than glass. Lenses and prisms made from sodium chloride are hence used by physicists in the study of infrared radiation. Needless to say such objects must be kept free from moisture.

Pure sodium chloride is not deliquescent, and shows little tendency to take up water vapor. The moistness characteristic of some table salt in humid weather is due to the presence of small amounts of calcium and magnesium chlorides, which have a great affinity for water vapor.

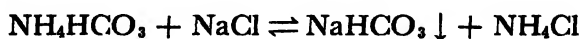
Another property of salt which makes it of value is its ability to lower the melting point of ice when it is added to the latter, causing the ice to melt if the salt solution formed has a freezing point lower than the air temperature at the time. A crude product, cheaper than table salt, is used for this purpose. While such treatment is useful in overcoming slippery sidewalks and streets in the wintertime, it has the disadvantage that the result-

ing salt solutions increase corrosion of iron objects, such as automobile fenders. Many soluble substances will lower the freezing point of water, and therefore will be of use in melting ice, but salt is one of the cheapest and most effective substances that can be employed.

When salt is mixed with snow or ice it causes a drop in temperature. This property is used in making mixtures for cooling purposes, as in the freezing of ice cream in the home. A mixture of one part of sodium chloride and three parts of snow will produce a temperature as low as -21°C . However, calcium chloride is more effective. Ten parts of the hydrate $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ mixed with seven parts of snow will produce a freezing mixture having a temperature as low as -55°C .

Chemical Properties of Salt. Sodium chloride is not a chemically reactive substance in the home. Its uses, improving the taste of food, melting ice, and providing freezing mixtures, do not involve chemical changes other than ion hydration. However, one might consider that it undergoes chemical changes in the body, since to some extent its ions become separated and replaced, as in its conversion to hydrochloric acid in the stomach.

In the industrial field sodium chloride is employed in a number of ways. One important process (Solvay) involves its conversion to sodium bicarbonate. When saturated sodium chloride solution reacts with ammonium bicarbonate an exchange of ions takes place, leading to a partial precipitation of sodium bicarbonate.



The precipitate is filtered off and in part sold as the familiar baking soda, while the remainder is converted by heat to the widely used industrial chemical soda ash (sodium carbonate, Na_2CO_3).



Much salt is also electrolyzed, in a process which will be described later, yielding sodium and chlorine, and in presence

[illegible]

Corp 1943 by Morton Salt Company.
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Shown on this chart are examples of the more than fourteen hundred uses of salt

of water sodium hydroxide, hydrogen, and chlorine, all industrial chemicals of great importance.

Salt in the Human Body. Sodium chloride is one of the substances which must be taken into the body if a state of health is to be maintained. Experiments have shown that when it is omitted from the diet progressively severe symptoms develop. Experimental animals kept on a salt-free diet tend to retain what salt they have, but if this is forced from their bodies by use of diuretics, irritability, weakness, shivering, paralysis, and death follow. Human beings with salt deficiency less than this may suffer from cramps, loss of appetite, sweating, and lassitude. On the other hand an excess of salt, particularly in the case of children, may bring on a temperature rise known as "salt fever." Ordinarily, however, a considerable amount of salt over that actually needed by the body can be tolerated. Excess salt is not immediately eliminated. It is apparently stored for a time in various places, the most important of which appears to be the skin. When the salt content of the body is high a greater amount of water is retained. One's weight may therefore be somewhat influenced by the amount of salt he consumes.

Loss of fluid of any kind by the body, such as perspiration, tears, or urine, is accompanied by a corresponding loss of salt. A human being loses a minimum of about two grams of salt daily in this way. This may be replaced entirely by the salt naturally present in the food eaten, but today it is customary, at least in prosperous countries, to add extra salt also, so that as much as eight or nine times the two-gram minimum may be consumed per day. Sodium chloride is present to a greater extent in meat than in vegetables and other plants. Consequently among the world's peoples meat eaters do not crave the substance as much as do the vegetarians. However, this is true only if the meat is roasted, or eaten raw, since boiled meat tends to lose its salt. It is thought that man's use of additional salt may have begun when he stopped his nomadic ways and took up agriculture, because his diet shifted at that time from

one based upon meat to one consisting largely of plant food. Animals behave similarly, and the vegetarians (c.g., deer) crave free salt more than meat eaters like dogs and cats.

This craving for salt has been present, therefore, a long way back in history; because of it ancient trade routes were developed for its transportation (as in Libya and Italy) and wars fought for possession of its sources. It has even been used for money (Abyssinia, Tibet).¹

THE CONSTITUENTS OF SALT

Salt is made up of the ions of sodium and chlorine, and by proper treatment it is possible to obtain the two elements in the free state from this source. The preparation, properties, and uses of these will be discussed briefly because they are among our most characteristic examples of metals and nonmetals.

Electrolysis. To obtain sodium and chlorine from common salt the latter is melted, two electrodes are inserted into the fluid, and an electric current is passed through, in a procedure known as an *electrolysis*. Since an electric current is a moving stream of electrons, the power source causes a piling up of electrons at one electrode, giving it a negative charge, and a drawing away of electrons from the other electrode, causing it to be positive.

The negatively charged electrode (the cathode) now attracts positively charged sodium ions to it. When these reach the electrode they each take up an electron and become atoms of metallic sodium, a substance with very different properties from sodium ions. Chloride ions go to the positive electrode (the anode) and give up their extra electrons, forming free chlorine atoms. These then join up in pairs to form covalent molecules of chlorine gas, which is also a substance with properties quite different from those of chloride ions.

The changes can be expressed by use of equations.



¹ Look up the etymology of the word "salary."

The result of this somewhat complicated mechanism is that electrons leave the cathode and go to the anode, just as if they had traveled directly from one to the other. The process therefore causes the circuit to be completed, and an electric current

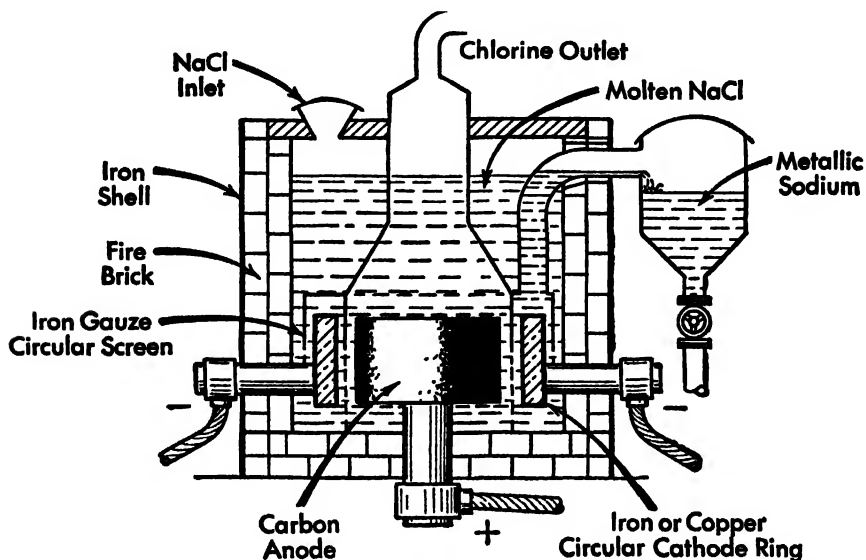


FIGURE 6.11. The Downs Cell for Producing Metallic Sodium and Chlorine Gas. From Sisler, Vander Werf and Davidson, *General Chemistry; A Systematic Approach*. Copyright, 1949, by The Macmillan Company.

flows. The metallic sodium and the chlorine gas must be kept apart, because otherwise they would quickly react to form sodium chloride again.



Sodium. Sodium is a soft, silvery metal which has the properties shown in Table 6.1.

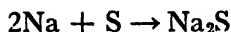
The atomic structure is typically that of a metal in that the number of electrons in the outermost shell is small (one, for sodium).

Sodium is a reactive metal, so much so that it is kept in an inert atmosphere, or under kerosene or toluene; it quickly tarnishes in the air. The compounds which it forms in its reactions are electrovalent in character. Equations for its combinations

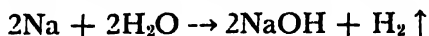
TABLE 6.1 Properties of Sodium

ELECTRON ARRANGEMENT	Two electrons in inner shell, eight in middle shell, one in outer shell.
MELTING POINT	97.5°C.
BOILING POINT	880°C.
DENSITY	0.97 gram per ml.
HEAT CONDUCTANCE RELATIVE TO MERCURY.	About 16 times as conductive as mercury
ELECTRICAL CONDUCTANCE	Excellent. Our cheapest conductor on a volume basis.
CHEMICAL REACTIVITY	Highly reactive. Combines with oxygen, hydrogen, chlorine, sulfur, phosphorus, etc. Displaces hydrogen from water, ammonia, acids.
PRICE	About 18 cents per pound.

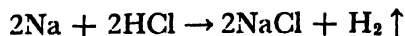
with oxygen and chlorine have already been given. As further examples of its reactivity, it combines with sulfur.



The metal violently displaces hydrogen from water,



and from acids such as hydrochloric acid.



Metallic sodium, once a laboratory curiosity, is today manufactured in such quantities that it is shipped in tank car lots, and its price is now close to that of copper. It is used both in the metallic state and as a reactant in the manufacture of various compounds.

The metal is employed as such in sodium vapor lamps, because of the inexpensive, low glare, yellow light which is emitted during the deactivation of the single outermost electrons of sodium atoms. The metal is also used in the exhaust valves of heavy duty gasoline engines. It aids in cooling these valves because the melted metal, flowing and splashing back and forth, carries

heat away from the surfaces exposed to hot gases. Sodium has replaced mercury in this respect because of its much better heat conductance (see table of properties). Another use for the metal is to conduct electricity. An iron-encased sodium rod is sometimes employed for carrying high amperage current.

Large amounts of sodium are used up in making sodium compounds such as the peroxide (Na_2O_2) and the amide (NaNH_2), and in the preparation of certain organic compounds, such as tetraethyl lead ($\text{Pb}(\text{C}_2\text{H}_5)_4$, page 324) and synthetic indigo.

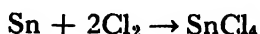
Chlorine. Chlorine is a greenish-yellow gas (actually a vapor) under room conditions. It has the properties shown in Table 6.2.

TABLE 6.2 Properties of Chlorine

ELECTRON ARRANGEMENT	2 electrons in inner shell, 8 in middle shell, 7 in outer shell.
MELTING POINT	-102°C .
BOILING POINT	-34.6°C . (one atmosphere pressure)
CRITICAL TEMPERATURE	144°C .
DENSITY	3.2 g./liter (gas at 0°C .) 1.56 g. ml. (liquid at -34°C .)
CHEMICAL REACTIVITY	Very reactive. Combines with most metals and many nonmetals. Reacts with many compounds.
ODOR	Highly irritating. Chlorine is a corrosive gas which was employed as the first war gas.
WATER SOLUBILITY	Soluble to the extent of about one per cent by weight under room conditions. The solution finds wide use in the laboratory as the reagent "Chlorine Water."

Chlorine is a typical nonmetal, with seven electrons in its outermost shell. Most nonmetals have more than half the maximum number of eight in this shell. The free element is very active, and forms both covalent and electrovalent compounds. Thus, covalence is exhibited in the chlorine molecule itself, $:\ddot{\text{Cl}}:\ddot{\text{Cl}}:$, while in salts like sodium chloride the element is elec-

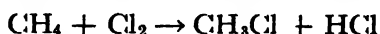
trivalent. It is a general property of chlorine to react with metals. For example, with tin it forms stannic chloride, a colorless, fuming liquid.



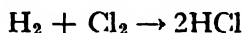
This reaction is used in recovering tin from tin cans. Chlorine combines with other nonmetals, such as phosphorus.



It reacts with many compounds, as with methane.

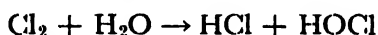


A well-known reaction is that with hydrogen.



The gaseous product, hydrogen chloride, dissolves in water to form the important chemical hydrochloric acid.

Chlorine reacts with water to form hydrochloric acid (HCl) and hypochlorous acid (HOCl).



Hypochlorous acid and its salts, chiefly sodium hypochlorite (NaOCl) and calcium hypochlorite ($\text{Ca}(\text{OCl})_2$) are widely used as antiseptics and bleaching agents. The oxygen in the hypochlorite radical (OCl) is capable of destroying bacteria, and of oxidizing many colored substances to colorless ones.

Bleaching agents used in the home and in industry are usually chemical substances containing the hypochlorite radical. These include bleaching powder, containing $\text{Ca}(\text{OH})\text{OCl}$; H.T.H. (high test hypochlorite) containing $\text{Ca}(\text{OCl})_2$; Javelle water and Clorox, containing NaOCl ; and many other similar substances sold under different proprietary names. Sodium chlorite (NaClO_2) is also used in the same way.

When any of these products is employed for bleaching cloth great care must be taken to avoid long exposure to the bleaching agent because of its weakening effect on the fibers, and after the bleaching all chemicals must be thoroughly washed from the cloth.

About 85 per cent of our manufactured chlorine is utilized for bleaching, and over two-thirds of this for bleaching paper pulp. Another important use of chlorine is for the sterilization of drinking water and swimming pool water. All types of harmful bacteria are destroyed by a concentration of two parts of chlorine, or less, per million parts of water. Chlorine is also employed in the manufacture of many important chemicals, including drugs, dyes, insecticides, antiseptics, refrigerants, and metallic and non-metallic chlorides.

Elements Similar to Sodium and Chlorine. There are five other metals with outer electron shells similar to that of sodium: lithium, potassium, rubidium, cesium, and francium. Little has been learned about the recently prepared, radioactive francium, but the remaining are well-known elements, rather similar to sodium in many of their properties. Lithium is used to some extent in removing impurities from iron and copper. Potassium, rubidium, and cesium are employed in photoelectric cells. Cesium is also used to remove traces of oxygen from electric lamps and radio tubes. These metals, including sodium, are all found in group I of the periodic system. They are known as the alkali metals.

Four other elements, fluorine, bromine, iodine, and astatine, have seven electrons in their outermost shell, like chlorine. Radioactive astatine, like francium, is not yet well known, but the remaining three elements have long been familiar to chemists. Compounds of fluorine are used for etching glass (hydrofluoric acid, H_2F_2), for insecticides (cryolite, Na_3AlF_6), and for refrigerants (Freon, CCl_2F_2). Bromine compounds are used in photography (silver bromide, AgBr), in making leaded gasoline (ethylene bromide, $\text{C}_2\text{H}_4\text{Br}_2$), and in dyes, drugs, and many other chemicals. Iodine, dissolved in alcohol, is used as an antiseptic (tincture of iodine) and as iodoform (CHI_3) for the same purpose. It is employed in photography (silver iodide, AgI), and in some dyes and drugs. The four elements fluorine, chlorine, bromine, and iodine are known collectively as the

halogens. They fall in group VII of the periodic system. The properties of these seven elements are given in Tables 6.3 and 6.4.

TABLE 6.3 Properties of Elements Similar to Sodium

	<i>Lithium</i>	<i>Potassium</i>	<i>Rubidium</i>	<i>Cesium</i>
ATOMIC WEIGHT	6.94	39.10	85.48	132.91
ATOMIC NUMBER	3	19	37	55
APPEARANCE (room temperature)	— ALL SILVERY METALS —			
DENSITY	0.53	0.86	1.58	1.90
MELTING POINT	186°C.	62.3°C.	38.5°C.	28.5°C.
BOILING POINT	1336°C.	760°C.	700°C.	670°C.
CHEMICAL ACTIVITY	— ALL HIGHLY ACTIVE —			
ELECTROVALENCE	— ALL HAVE ELECTROVALENCE OF PLUS ONE —			

TABLE 6.4 Properties of Elements Similar to Chlorine

	<i>Fluorine</i>	<i>Bromine</i>	<i>Iodine</i>
ATOMIC WEIGHT	19.00	79.916	126.92
ATOMIC NUMBER	9	35	53
APPEARANCE (room temperature)	pale greenish-yellow gas	reddish-brown liquid	black solid
DENSITY	1.7 g./liter (gas at 0°C.)	3.1 g./ml. (liquid)	4.9 g./ml. (solid)
MELTING POINT	−223°C.	−7.2°C.	113.5°C.
BOILING POINT	−187°C.	58.8°C.	184.4°C.
CHEMICAL ACTIVITY	highly active	active	moderately active
ELECTROVALENCE	— ALL NEGATIVE ONE —		

Self Study Questions

1. Where does sodium chloride occur in nature? How do we account for deposits of solid sodium chloride?
2. Describe two methods for obtaining salt from underground deposits.
3. What are the atomic structures of (a) neutral sodium and chlorine atoms, (b) sodium and chlorine ions?
4. Account for the change which takes place when metallic sodium and chlorine gas react. What force holds the ions together in sodium chloride?

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5. Define electrovalence. Explain how it differs from covalence. Can an element exhibit both electrovalence and covalence? Example.

6. How are the ions arranged in solid sodium chloride? What shape does this cause in salt crystals?

7. What are some of the physical properties of sodium chloride? Illustrate with an equation at least one chemical property of this substance.

8- Discuss the importance of salt in the human body.

9. Give at least four uses for salt in the home.

10. What is an electrolysis? Describe what happens when sodium chloride is electrolyzed. What is the anode? The cathode?

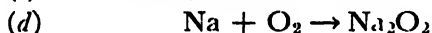
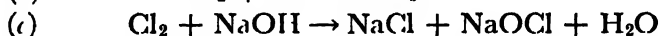
11. What volume of chlorine gas (standard conditions) could theoretically be obtained by the electrolysis of 585 grams of sodium chloride?

Answer: 112 liters.

12. Give several physical and chemical properties of the elements sodium and chlorine. Name at least six uses for these substances.

13. Name four elements similar to sodium, and three similar to chlorine. Where are these elements found in the periodic system?

14. To gain experience, the reader may wish to balance the following equations.



VII

Electrolytes; Ionization

General Properties of Electrolytes. The substances acids, bases, and salts go under the general heading of *electrolytes*.¹ While there are characteristic differences between acids, bases, and salts which will be described below, as electrolytes they have several properties in common. They are all to some degree electrovalent substances, or become so in the presence of water. This leads to a generalization which aids in learning; all of the formulas of these substances can be considered as consisting of a positive part and a negative part, and knowledge of a few of these part formulas (radicals) permits the student to reason out a large number of electrolyte formulas. Many electrolytes are soluble in water, giving solutions which conduct electricity for the same reason that the molten sodium chloride mentioned in the last chapter conducted electricity; freely moving ions are attracted to the electrodes, and upon arrival they remove electrons from one electrode and deposit them at the other. To behave in this manner it is apparent that the electrolyte in water solution must be broken up (dissociated) into positive and negative ions which can move about independently of each other.

Dissociation. The dissociation of electrolytes in solution was first suggested by Arrhenius (Swedish) as a theory, in 1887, to account for the electrical conductivity of these solutions and other facts which could not be explained satisfactorily at that

¹ From the Greek *elektro-*, denoting electricity, and *-lytos*, dissolve 1; hence, a substance which conducts electricity when dissolved.

time, such as abnormal² freezing point lowering and boiling point rise, and the simple exchange of radicals which so often occurred when electrolytes in solution reacted with one another.

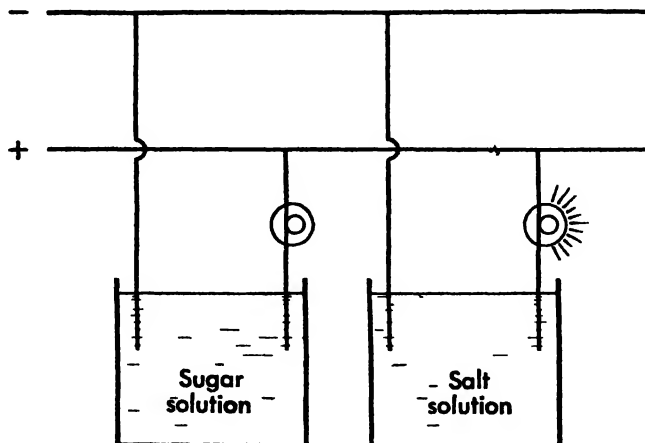


FIGURE 7.1. Electrolyte and Nonelectrolyte Solutions. Salt and other electrolytes in water solution conduct electricity, as shown by the lighting of a lamp in the circuit. Nonelectrolytes such as sugar do not conduct electricity in solution.

Arrhenius's ionization theory explained these things so well that it was generally accepted, after a period of passive resistance. The dissociation of electrolytes in solution is now regarded as a fact rather than as a theory

In his original theory Arrhenius imagined the ions to be formed at the time of the dissociation, whereas we now believe,

² A gram molecular weight of a nonelectrolyte such as table sugar (342 g.) or methyl alcohol (32 g.) dissolved in 1000 g. of water freezes at $-1.86^{\circ}\text{C}.$ and boils at $100.52^{\circ}\text{C}.$ (one atmosphere pressure). These values are the *normal* freezing and boiling points for such solutions. They are virtually constant, in spite of the great variation possible in gram molecular weights, because the lowering of the freezing point and the rise of the boiling point produced are proportional to the concentration, i.e., to the number of molecules of nonelectrolyte per 1000 grams of water. This number is the same for a gram molecular weight of any nonelectrolyte, 6.023×10^{23} molecules. On the other hand, when a gram molecular weight of an electrolyte such as salt is so dissolved, the freezing point of the resulting solution is lower than $-1.86^{\circ}\text{C}.$, and the boiling point at one atmosphere pressure is higher than $100.52^{\circ}\text{C}.$, hence these values are called *abnormal*. The explanation is that dissociation causes the number of dissolved particles (ions, molecules) to be greater than 6.023×10^{23} .

in the case of many electrolytes, that the ions are present as such in the undissolved electrolyte, as for example those which make up the sodium chloride crystals described in the last chapter.

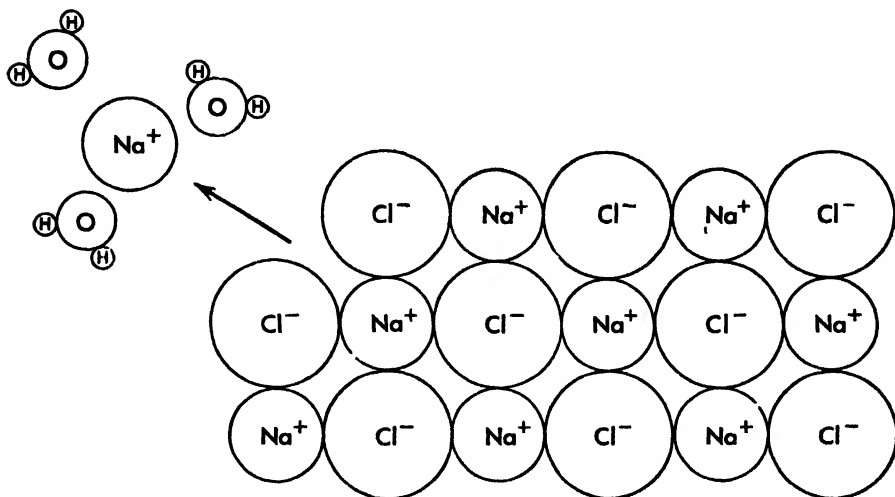


FIGURE 7.2. Dissolving of Electrolytes. A separation of ions takes place when strong electrolytes dissolve, aided by the attraction between the ions and water molecules, and by thermal and other movements.

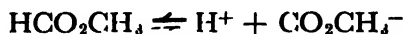
The term “dissociation” is then perhaps preferable for describing the ion separation which occurs when these electrolytes are dissolved in water, rather than Arrhenius’s term “ionization,” since the latter process has already taken place at the time of formation of the electrovalent compound.

Dissociation in solution is thought to occur because the electrolyte ions have a greater affinity for water than they have for each other. Thus, when sodium chloride dissolves in water, molecules of the latter substance are visualized as coming between the sodium and chloride ions in the salt crystal, or at least weakening the electrovalent bond between them, with the result that the crystal separates into its component ions, each of which is thereafter associated with one or more water molecules as an independent unit which moves rather freely throughout the solution. However, it appears that a slight attraction still exists between positive and negative ions, because electrolyte

solutions of this type do not quite behave experimentally as if the dissociation were 100 per cent.

Electrolytes which are highly or completely dissociated in solution are called *strong*, and those which separate into ions to only a small extent are designated as *weak*. For example, hydrochloric acid, sodium hydroxide, and most salts are strong electrolytes, while ammonium hydroxide and acetic acid are weak.

Equilibria in Weak Electrolyte Solutions. In solutions of weak electrolytes an equilibrium exists between the ions and the undissociated substance. Thus, with acetic acid:



One of the double arrows used in this equation is seen to be heavier than the other. This convention is employed to show that the equilibrium is displaced in one direction or the other, i.e., that there is not just an equal quantity of reactants and products. The heavier arrow points to the substance or substances present in greatest amount at equilibrium. In the case of acetic acid in dilute solution approximately 98 per cent of the substance remains in undissociated form.

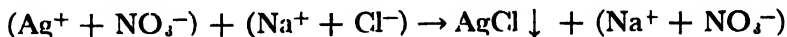
In such ionic equilibria, like all equilibria encountered in chemistry, both of the processes involved continue to take place after equilibrium is reached. In the acetic acid solution just discussed, for example, acetic acid molecules continue to separate into ions, and the ions continue to combine and reform acetic acid molecules. These equilibria are therefore *dynamic*, rather than *static* in nature, and a state of equilibrium is maintained only because the two processes happen to be taking place at the same rate.

It is difficult for beginning chemistry students to understand how an equilibrium can be reached in such situations, as for example when 98 per cent of reactants, and only 2 per cent of products, are present. The process can perhaps be made clearer by using the nut and bolt analogy mentioned earlier (page 9). One might imagine a room with the floor covered with a

mixture of nuts, bolts, and combinations, the latter each consisting of a nut screwed on a bolt. Suppose further that two men are working as rapidly as they can in this room—one to separate all the combinations into individual nuts and bolts, the other to make combinations out of individual nuts and bolts.

Let us assume that the man putting the combinations together is the faster of the two. As time passes a greater and greater number of combinations are formed and fewer and fewer individual nuts and bolts remain. However, a limiting factor now appears. There are eventually so few nuts and bolts remaining that the faster man must spend time looking for them, whereas the other man can reach anywhere and find a combination to take apart. The faster man is slowed up, and eventually their rates become the same. *Equilibrium* is reached, even though nearly all of the nuts and bolts have been converted to combinations. In much the same way we account for the equilibrium in the acetic acid solution, even though only about 2 per cent of the acid is dissociated. The ions tend to combine more readily than the molecules tend to dissociate, but so few ions remain at equilibrium that they meet relatively infrequently.

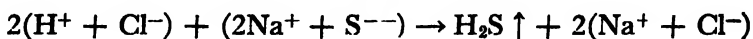
Reactions Between Electrolytes. When solutions of different electrolytes are mixed, a reaction sometimes takes place between oppositely charged ions. For example, if silver nitrate solution is added to sodium chloride solution a white, insoluble substance, silver chloride, is formed.



Chemical changes of this sort are known as *ionic reactions*, and also as *double decompositions* when the process is a simple exchange of ions, as in the example above. The conventions employed in writing such equations should be explained. Electrolytes dissociated in solution are written with the ions separated, as $(\text{Ag}^+ + \text{NO}_3^-)$, whereas when the substance is not in solution, but exists as a solid, liquid, or gas, the associated formula is used, such as AgCl . The arrow pointing down after the formula

for silver chloride is a convention used to show that this substance precipitates. A line is sometimes drawn under the formula of the precipitating substance to mean the same thing, e.g., AgCl.

Precipitate formation is not the only cause of such ionic reactions. An insoluble gas may be formed, as in the reaction between hydrochloric acid and sodium sulfide.



Hydrogen sulfide gas escapes, as indicated by the arrow pointing upward. Gas formation is also shown by a line drawn over the formula, e.g., $\overline{\text{H}_2\text{S}}$.

A third cause for such reactions is the formation of an undissociated soluble substance. For example, when barium hydroxide and nitric acid react, barium nitrate and water are formed. The water is virtually undissociated.



Complete and Incomplete Ionic Reactions. Ionic reactions of the kinds just described would be expected to go to completion, rather than to reach a state of equilibrium, if the precipitate or gas were completely insoluble, or if an entirely undissociated substance were formed. No equilibrium would be possible because two of the types of ions necessary for the back reaction would have been taken from the solution by the formation of the product in question.

However, very few ionic reactions actually go entirely to completion, since even our most insoluble substances are not completely insoluble, nor is a product like water entirely undissociated. The reactions in the examples above go *virtually* to completion, and are considered as completed reactions for most practical purposes. Since they are so considered, it is usually customary to use a single arrow as shown, rather than the double arrow employed in reactions in which the point of equilibrium is not displaced so far in one direction or the other.

On the other hand, many ionic reactions are far from complete,

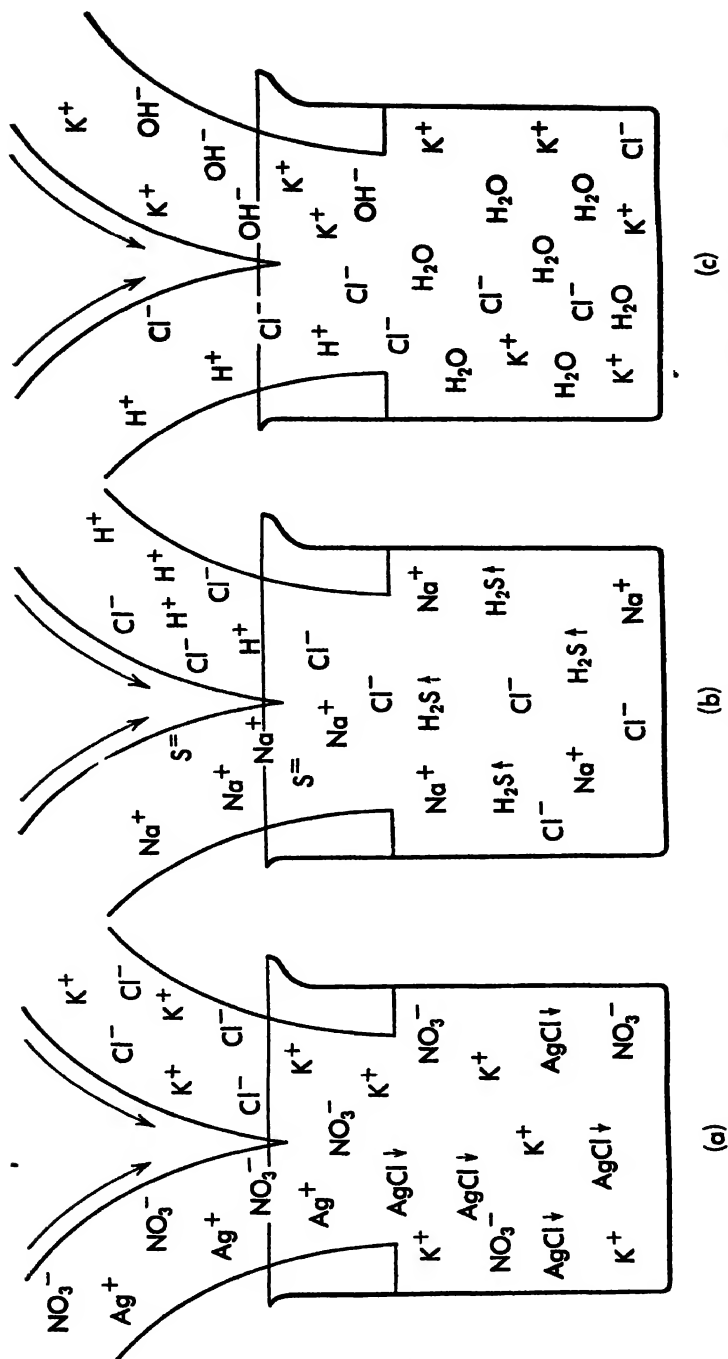
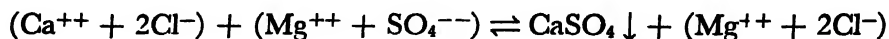


FIGURE 7 3 Completed Ionic Reactions (a) An insoluble solid is formed (b) An insoluble gas is formed. (c) An undissociated substance is formed.

and in this case double arrows are utilized. For example, when sufficiently concentrated solutions of calcium chloride and magnesium sulfate are mixed a partial precipitation of calcium sulfate occurs.



At equilibrium the calcium sulfate crystals which make up the precipitate are continually being formed by deposition of ions from the solution and they are also continually dissolving. The rates at which these two processes take place are the same, hence a state of equilibrium exists. The point here is that since calcium sulfate is appreciably soluble, significant numbers of the ions shown on the left-hand side of the equation above are always present. This reaction does not go virtually to completion in either direction.

Let us now consider in turn each of the three classes of electrolytes.

A C I D S

Acids can be considered for present purposes as substances which dissociate in water solution to yield *hydrogen ions*³ and one of the many types of negative ions or *anions*. A few of the common anions are given in Table 7.1 on page 162. The dissociation takes place because the ions of the undissociated electrolyte prefer to attach themselves to water molecules rather than to each other. This tendency, together with the molecular movements always present in such solutions, accounts for the separation of the ions. The latter are therefore hydrated in solution (as for example the hydronium ion, page 117), but for simplicity the water will usually be omitted when they are written. Thus, hydrochloric acid is dissociated in solution into hydrogen and chloride ions.

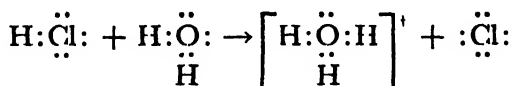


³The more general definitions of acids and bases proposed by Brönsted and Lowry, and by Lewis, will not be discussed or used in this text, since only aqueous systems are described; hence, the acids and bases of importance to the beginning chemistry student are adequately characterized, in the author's opinion, by the older definitions employed here.

The same reaction is described below in more detail to show the role which water plays in such dissociations.

The presence of hydrogen ions in solution causes certain characteristic properties to appear. The solutions taste sour. The colored substance litmus is turned from blue to red, by even as little as a few millionths of a gram molecular weight of hydrogen ion per liter. Because hydrogen ions are present acid solutions also react with bases to form salts, in a chemical change known as a neutralization, which will be described later. Some important inorganic acids will now be discussed. .

Hydrochloric Acid. This substance is prepared by dissolving the gas hydrogen chloride (see page 139) in water. The molecules which make up the gas are covalent, i.e., $\text{H}:\ddot{\text{Cl}}:$. However, when they dissolve in water, hydrogen ions, or protons (*not* neutral hydrogen atoms) are drawn away from the hydrogen chloride molecules by water molecules, leaving chloride ions, and a solution with strong acid properties results.



Or, as it is sometimes written without showing hydration:



Hydrochloric acid is a colorless solution whose boiling point varies with pressure and percentage of hydrogen chloride, but reaches a maximum of $110^\circ\text{C}.$ at atmospheric pressure when the solution contains 20.2 per cent of the gas. The solution commonly supplied to laboratories contains about 37 per cent hydrogen chloride. At this strength it has a density of 1.19 and fumes in moist air because of the escape of hydrogen chloride. The latter gas takes up water and forms a fog of hydrochloric acid droplets.

The acid has the general properties, given above, of this class of substances, and in addition it has specific properties due to the presence of the chloride ion, e.g., it reacts with metal oxides, hydroxides, and with some salts to form chlorides.

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- (1) $(\text{H}^+ + \text{Cl}^-) + (\text{Na}^+ + \text{OH}^-) \rightarrow (\text{Na}^+ + \text{Cl}^-) + \text{H}_2\text{O}$
- (2) $2(\text{H}^+ + \text{Cl}^-) + \text{CuO} \rightarrow (\text{Cu}^{++} + 2\text{Cl}^-) + \text{H}_2\text{O}$
- (3) $(\text{Ag}^+ + \text{NO}_3^-) + (\text{H}^+ + \text{Cl}^-) \rightarrow (\text{H}^+ + \text{NO}_3^-) + \text{AgCl} \downarrow$

The last reaction is used to detect chlorides in water solutions. Silver chloride forms as a white precipitate insoluble in dilute nitric acid.

Hydrochloric acid is second only to sulfuric acid among the important industrial acids. Large quantities are used in cleaning steel preparatory to coating it with zinc or tin. It is employed in the manufacture of dyes and other organic compounds. It is used in making corn syrup from corn starch (see page 368). It is a common laboratory reagent.

Sulfuric Acid. This is our most important industrial acid, and indeed, our most widely used manufactured chemical (about ten million tons per year, in this country). The acid is prepared industrially by either the lead chamber process or the contact process, the latter being chemically the simpler of the two. In this method sulfur (usually) is burned in air to yield sulfur dioxide. This in turn reacts with more oxygen in the presence of a catalyst to form sulfur trioxide and the latter is indirectly combined with water to form sulfuric acid. Thus:

- (1) $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$
- (2) $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$
- (3) $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

The product is pure, largely because the reactants are purified before use to prevent the catalyst from becoming poisoned (rendered ineffective). See Figures 7.4 and 7.5.

The sulfuric acid of commerce contains approximately 95 per cent pure hydrogen sulfate (H_2SO_4) and has a density of about 1.83 g. per ml. The concentrated acid begins to lose sulfur trioxide at about 150°C . but the loss is small, and the acid can be heated to well over 300°C . before it begins to decompose rapidly. The viscosity of the acid is greater than that of water. It is approximately that of mineral oil; hence, the acid appears

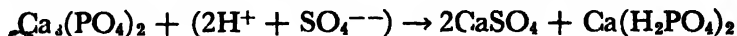


FIGURE 7.4. Overall View of Contact Plant for Sulfuric Acid Sulfur is burned to sulfur dioxide in burner at extreme left. Sulfur dioxide is further oxidized to sulfur trioxide in reactors employing vanadium oxide catalyst on both sides of the coke-bed filter in the center of the photograph Sulfur trioxide is later combined indirectly with water to yield sulfuric acid. Courtesy Monsanto Chemical Company.

to be oily when shaken, and for this reason it is sometimes called oil of vitriol, a name coming down to us from antiquity. Sulfuric acid has been used in commercial amounts for about 200 years.

The substance is of such importance because of its cheapness, and because of the following four properties:

(1) In the presence of water it is a moderately strong acid. Thus, the dilute acid reacts with calcium phosphate.

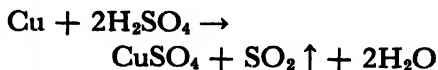


The calcium hydrogen phosphate produced is an acid salt (see below) which is sufficiently soluble in water to make it of great value in fertilizers, and the above reaction accounts for the greatest single use of sulfuric acid, to the extent of nearly three million tons yearly.

(2) It is an oxidizing⁴ agent. With copper, for example, it reacts to form copper sulfate, sulfur dioxide, and water. The acid must be concentrated.

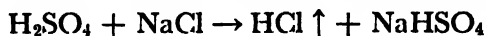


FIGURE 7.5. Sulfuric Acid Manufacture. Sulfur trioxide from the contact plant in Figure 7.4 is made to combine with water in the presence of sulfuric acid. This process liberates a great deal of heat, and the final product, sulfuric acid, must be cooled in the manner shown above. Courtesy Monsanto Chemical Company.



(3) In concentrated form it is a good dehydrating agent. It is used in connection with nitric acid in forming such products as cellulose nitrate (page 380) and TNT (page 343), since it removes the water which results from the reactions with nitric acid and thus enables the reaction to go more readily to completion.

(4) It has a high boiling point, or more accurately a high decomposition temperature, as was mentioned earlier. It can therefore be used to displace other acids in anhydrous form from their salts. For example, one of the principal methods of preparing hydrogen chloride for use in making hydrochloric acid is by treating common salt with sulfuric acid.



At low temperatures the more volatile hydrogen chloride comes off and sodium acid sulfate remains.

Sulfuric acid is used in the cleaning ("pickling") of steel surfaces before application of various protective coatings. It is employed in making many organic compounds, particularly

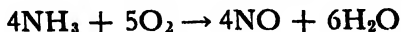
⁴ An oxidizing agent is one which causes another element to undergo a change of valence number in a positive direction, e.g., copper changes in valence from zero to two. See page 263.



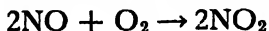
FIGURE 7.6. Concentrated Sulfuric Acid Is Shipped in Tank Cars, Courtesy Monsanto Chemical Company

dyes, explosives, and drugs. Large quantities are required in the making of fertilizers and in the refining of oil. It is used in the manufacture of many inorganic chemicals besides the hydrogen chloride mentioned above. It is utilized in electrolytic baths employed for the refining of metals such as copper and zinc. It also has many other uses.

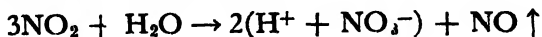
✓ **Nitric Acid.** Nearly all of this important acid is now obtained from ammonia. The latter is mixed with excess air and passed over a heated platinum catalyst whose temperature is maintained by the heat liberated during the ensuing oxidation.



The nitric oxide gas is cooled, whereupon it combines with more oxygen from the excess of air present.



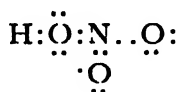
The nitrogen dioxide gas is then carried to an absorption tower, where it reacts with warm water.



Two-thirds of the nitrogen dioxide is converted to nitric acid by this step. The nitric oxide formed then combines with more oxygen, yielding more nitrogen dioxide, which again reacts with water as before, etc.

Nitric acid is supplied to laboratories as a colorless or nearly colorless liquid which contains about 70 per cent HNO_3 and has a density of 1.4 g./ml. Another manufactured product, brownish in color because of dissolved nitrogen dioxide, is fuming nitric acid. It is nearly pure hydrogen nitrate, and is a stronger oxidizing agent than the ordinary acid.

The two outstanding properties of nitric acid are that it is a strong acid and a good oxidizer. The acid properties are shown in water solution. The most pronounced oxidizing properties are exhibited by the water-free substance, which probably has the covalent structure shown. However, even in the presence of some

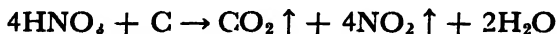


water nitric acid is still able to oxidize. Consider the following examples of these two properties.

As an acid, nitric acid will react with the base calcium hydroxide to form calcium nitrate and water (neutralization, page 160).



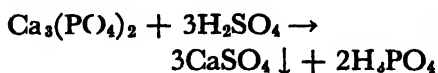
As an oxidizing agent, it converts carbon to carbon dioxide.



The subject of oxidation will be described more fully under copper (page 263).

Nitric acid has many industrial uses, in the manufacture of explosives, plastics, dyes, drugs, and fertilizers. It is also a common laboratory liquid, employed as a dissolving and a neutralizing reagent.

✓ **Phosphoric Acid.** There are a number of acids of phosphorus, but of greatest importance is orthophosphoric acid, H_3PO_4 , usually called simply phosphoric acid. It is prepared by treating calcium phosphate with sulfuric acid. The calcium sulfate precipitates, and can be filtered off, leaving phosphoric acid in solution.



The solution supplied to laboratories is a somewhat viscous product containing about 85 per cent of H_3PO_4 . Three hydrogen ions would be expected to dissociate, from the formula. This is the case, but they differ

in ease, and hence in degree, of dissociation. The second hydrogen ion leaves more reluctantly than the first, and the third hydrogen ion still more so.



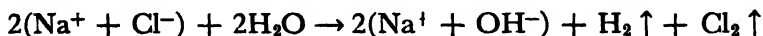
FIGURE 7.7. Phosphate Rock. Strip mining in Tennessee.

B A S E S

A base will be defined here as a substance which dissociates in water solution to yield the hydroxide ion and one of the many positive ions or *cations*. As in other electrolyte dissociations, water attracts the ions and hence brings about the dissociation. In the case of some bases water is required to furnish the oxygen atom of the hydroxide ion, as when ammonia is dissolved in water (see below). Present also must be a compensating number of positive ions (cations); it is these which determine the kind of a base under consideration. Because of the presence of the hydroxide ion, bases in solution taste bitter, feel slippery between the fingers, and turn red litmus blue. They also react with acids to form salts and water.

Sodium hydroxide and ammonium hydroxide are two important bases.

Sodium Hydroxide. Solid sodium hydroxide is a white, crystalline substance with a great affinity for water (deliquescent) and carbon dioxide. It is prepared by electrolysis of sodium chloride solutions. Thus:

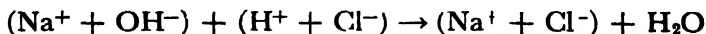


The solution of sodium hydroxide is kept separate from the chlorine gas, to avoid reaction between the two. Upon evaporation it yields solid sodium hydroxide. Hydrogen gas is also formed. A solution of common salt is thus the source of three highly important industrial chemicals (Figure 7.8).

Solid sodium hydroxide has a density of 2.13 g. per ml., melts at 318°C., and boils at 1390°C. It is very soluble in water, 42 grams at 0°C. and 347 grams at 100°C. dissolving in 100 grams of water. Its water solutions have the characteristic behaviour of strong bases, turning red litmus blue, feeling slippery between the fingers, and being bitter in taste. The substance is called caustic soda because of its injurious effect upon all living matter; upon contact the latter is disintegrated. Sodium hydroxide is probably completely dissociated in solution.



It neutralizes acids to form salts and water.



Sodium hydroxide is an important industrial chemical, produced in this country to the extent of more than a million tons a year. It is used in the production of rayon and soap, and in the treatment of petroleum, paper, rubber, vegetable oils, and textiles. It is also employed for cleaning drains and for other purposes in the home, under the name *lye*.



FIGURE 7.8. Hooker Cells for the Manufacture of Sodium Hydroxide Solution, Chlorine, and Hydrogen from Brine Solution by Electrolysis. Visible in front are sight glasses to determine brine levels and outlets for sodium hydroxide solution. Brine inlets and hydrogen and chlorine outlets are also part of these cells. Courtesy Monsanto Chemical Company.

Ammonium Hydroxide. This substance is formed when ammonia, NH_3 , is dissolved in water. It is a weak base, only a few per cent of the potential ions being present in dilute solutions. The ions are in equilibrium with ammonia and water.



The formula NH_4OH is often used for the undissociated base, and a hydrate of this composition can be obtained at low temperatures, but there is doubt as to its existence at ordinary temperatures. Some authorities believe the only products present in the solution are those shown in the equation above.

Ammonia solution is used as a cleaning agent, a water softener, and as a common laboratory reagent, employed for neutralizing acids and for other purposes.

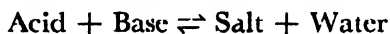
S A L T S

Salts are crystalline substances of electrovalent character made up from the anions of acids and the cations of bases. They are our largest class of electrolytes. They are formed, along with water, when an acid and a base react, in a process known as *neutralization*. Thus, when nitric acid and potassium hydroxide react, potassium nitrate and water are formed.

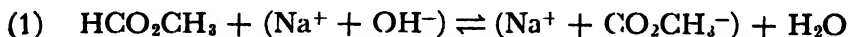


Normal salts contain neither hydrogen nor hydroxide ions in their crystals. However, salts are known which do contain one or the other of these, made by partial neutralization of an acid or a base. Sodium hydrogen sulfate (or sodium bisulfate), $NaHSO_4$, is an example of an *acid* salt, and basic magnesium chloride, $MgOHCl$, is an example of a *basic* salt.

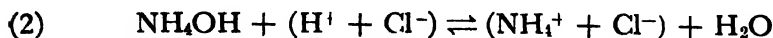
Hydrolysis. The neutralization reaction $Acid + Base \rightarrow Salt + Water$ is not always a completed one. If either the acid or the base happens to be a weakly dissociated electrolyte a back reaction occurs, and a state of equilibrium is reached.



When equivalent amounts⁵ of a weak acid and a strong base are mixed the resulting solution will therefore be basic at equilibrium because of the excess of hydroxide ions present. Such a solution is obtained, for example, by mixing equivalent amounts of acetic acid and sodium hydroxide solutions.



Conversely a strong acid-weak base mixture is acidic at equilibrium, as when hydrochloric acid is added to an equivalent amount of ammonium hydroxide solution. The latter is written NH_4OH for simplicity.



⁵ By equivalent amounts is meant quantities of each which would react completely with each other, with neither left in excess, if the reaction went to completion. See page 178 for a more detailed meaning of equivalent.

The weak dissociation of ammonium hydroxide, acetic acid, and water has been neglected in these equations.

The salts formed in such reactions cause similar equilibria to be reached if they are dissolved separately in water. Sodium acetate when put into solution reacts with water and causes an equilibrium similar to (1). Ammonium chloride gives an equilibrium like (2) when dissolved in water. Hence a sodium acetate solution is basic and an ammonium chloride solution is acidic.

The reaction of a salt with water in this way is called *hydrolysis*. Hydrolysis can then be conveniently thought of as the reverse of neutralization, i.e., as the back reaction which takes place, causing partial formation of a weak acid and/or a weak base, when a salt is dissolved in water. Only salts formed from weak acids or weak bases, or both, undergo significant hydrolysis in water solution. A salt such as sodium chloride, formed from hydrochloric acid (strong) and sodium hydroxide (strong), dissolves in water to form an essentially neutral solution.

FORMULAS OF ACIDS, BASES, AND SALTS

A simple rule is helpful in writing the formulas for electrolytes: *The total positive electrovalence of the cations in a formula must equal the total negative electrovalence of the anions*, since the whole compound must be electrically neutral. This is an extension of an earlier rule used for binary compounds (page 73). For example, the phosphate ion has an electrovalence of -3 , and the calcium ion an electrovalence of $+2$. The formula for calcium phosphate is then written $\text{Ca}_3(\text{PO}_4)_2$, since in this formula the total cation electrovalence, $+2 \times 3$, is numerically equal to the total anion electrovalence, -3×2 . It is usually customary in writing formulas of electrovalent substances to use the simplest possible ratio of radicals which correctly expresses the composition of the compound.

It is therefore to the reader's advantage to learn the common electrovalences of a few of the better known anions and cations, if he wishes to be able to write formulas and equations involving electrovalent substances correctly, because a great many formulas

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of acids, bases, and salts can be reasoned out from these few learned ions and valences, shown in Table 7.1.

TABLE 7.1* Ion Formulas and Valences

Cations			Anions		
Name	Formula	Electrovalence	Name	Formula	Electrovalence
SODIUM	Na	1	FLUORIDE	F	-1
POTASSIUM	K	1	IODIDE	I	-1
LITHIUM	Li	1	NITRATE	NO ₃	-1
AMMONIUM	NH ₄	1	CHLORIDE	Cl	-1
SILVER	Ag	1	HYDROXIDE	OH	-1
HYDROGEN	H	1	BROMIDE	Br	-1
MERCURY	Hg	1, 2	ACETATE	CO ₂ CH ₃	-1
(mercurous,† mercuric)			CHLORATE	ClO ₃	-1
COPPER (cupric)	Cu	2	HYPOCHLORITE	OCl	-1
CALCIUM	Ca	2	SULFATE	SO ₄	-2
LEAD	Pb	2	CARBONATE	CO ₃	-2
URANYL	UO ₂	2	OXIDE	O	-2
MAGNESIUM	Mg	2	SULFIDE	S	-2
ZINC	Zn	2	SILICATE	SiO ₃	-2
IRON (ferrous, ferric)	Fe	2, 3	CHROMATE	CrO ₄	-2
ALUMINUM	Al	3	OXALATE	C ₂ O ₄	-2
TIN (stannous, stannic)	Sn	2, 4	PHOSPHATE	PO ₄	-3

* This table includes only the common electrovalences of the most frequently used ions. If the reader likes to use associations as review aids the first letters of each column make nonsense expressions.

† The mercurous ion always occurs in double-atom form, Hg₂²⁺

Nomenclature. When the positive ions (cations) consist of single atoms having but one valence they are named the same as the elements, e.g., sodium, zinc. When two common valences exist the ending -ous is used for the lower valence form and -ic for the higher valence form, as for example mercurous and mercuric. In the case of iron and tin the Latin prefixes ferr- and stann- are used with these endings, rather than the common element names. The ending -ide is used for those anions which consist of but one kind of element, e.g., chloride, sulfide, oxide. An exception is the hydroxide ion, containing hydrogen and oxygen. Many of the anions form ions with a smaller negative

charge containing hydrogen. The commonest of these is probably the bicarbonate ion, HCO_3^- .

Electrolytes in the Home. A number of acids, bases, and salts are found in the home. The sour taste of vinegar is caused by acetic acid, oranges and lemons contain citric acid, and grapes, tartaric acid. Carbonic acid, H_2CO_3 , is present in soda water and other carbonated beverages. Lye (sodium hydroxide) and household ammonia (ammonium hydroxide), already described, are common bases found in the home. Slaked lime (calcium hydroxide, $\text{Ca}(\text{OH})_2$) is a sparingly soluble base whose solution is called lime water.

Table salt is probably the most widely used electrolyte in the home, unless one includes the colloidal electrolyte soap (Chapter XXIV). Other familiar salts are baking soda (sodium bicarbonate, NaHCO_3), washing soda (hydrated sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), borax (hydrated sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), TSP (trisodium phosphate, Na_3PO_4), soap, described later, and solutions of sodium hypochlorite (NaOCl). Chlorides, sulfates and bicarbonates of calcium, magnesium, and sodium are common impurities in natural water. Salts of lead, zinc, barium, and other metals are often present in the pigment part of paints.

While most electrolytes used in the home are not dangerous when employed in the proper manner, the reader should be familiar with hazards sometimes encountered. Lye is one of the most corrosive of poisons. Household ammonia is also toxic, and all soluble electrolytes are injurious if taken in excessive amounts, even table salt. Metals may be attacked by acids or alkalis. Aluminum and zinc are particularly easily damaged, or even dissolved, by sodium hydroxide solutions. The acid present in mayonnaise and salad dressing attacks metals in the presence of air.

The strength of cloth is in general lessened by contact with acidic or alkaline solutions, and by certain salt solutions, as sodium hypochlorite. Antimony, whose soluble compounds are

toxic, is dissolved out of some enamels, if present, by citric acid from citrus fruits. It is a good idea not to allow orange or lemon juice, or acidic solutions in general, to stand in contact with enamelware for long periods of time. Some paints contain metal salts which are soluble in the hydrochloric acid of the stomach. These may be injurious. A white lead (basic lead carbonate) pigment, for example, should not be present in paints or enamels used for children's toys, beds, etc. Toxic salts, such as lead arsenate, are sometimes present on the skin of fruit as spray residue. Poisonous antiseptics, such as phenol (carbolic acid) and bichloride of mercury, and toxic drugs, such as sodium pentobarbital, should be carefully kept out of reach of children.

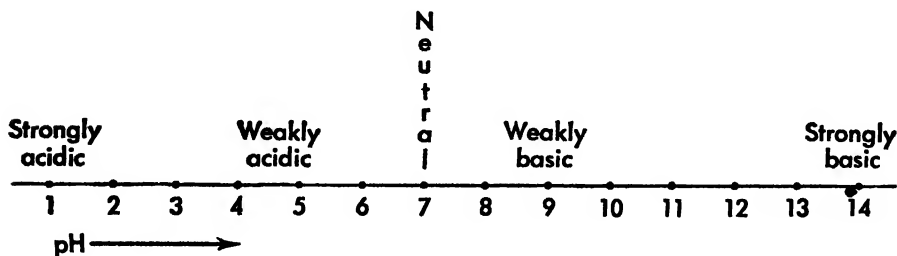


FIGURE 7.9. The pH Scale.

pH. The acidity or alkalinity of solutions can be quantitatively expressed in various ways. For example, an acid solution might be described as containing 0.0001 gram molecular weight of hydrogen ion per liter. A convenient, widely used method for showing such acidity or alkalinity is by the pH scale.⁶ This is a series of numbers, usually varying from zero to 14, in which 7 means a neutral solution at room temperature, values less than 7 are given to acid solutions and those greater than 7 to alkaline solutions. The greater the acidity or alkalinity the farther below or above seven is the number used, as shown in Table 7.2. Listed in Table 7.3 are the pH values of some common foods, beverages, and other fluids.

⁶ $\text{pH} = \text{Log}_{10} 1/a_{\text{H}^+}$, where a_{H^+} is the hydrogen ion activity, nearly the same in dilute solution as the concentration. The term pH is a combination of letters stemming from the words "potential of hydrogen," since the expression $\text{log}_{10} 1/a_{\text{H}^+}$ occurs in the mathematical equation used for calculating acidity from electrical data.

TABLE 7.2 pH and Hydrogen Ion Concentrations

pH	<i>Hydrogen ion concentration,* gram molecular weights per liter</i>
1	0.1
3	0.001
5	0.00001
7	0.0000001
	<i>Hydroxide ion concentration,* gram molecular weights per liter</i>
7	0.0000001
9	0.00001
11	0.001
13	0.1

TABLE 7.3 pH of Various Substances

NATURAL WATER	5-10 (usually close to 7)
MILK	6.6-6.8
BLOOD	7.35-7.45
URINE	5.5-7.5
LEMON JUICE	2.0-2.1
GRAPEFRUIT JUICE	2.9-3.2
ORANGE JUICE	3.3-4.3
TOMATO JUICE	4.1-4.3
EGG WHITE	8.0-9.0
EGG YOLK	6.1-7.8
CLEAR COFFEE	4.7-5.0
CLEAR TEA	5.0-7.0
CARBONATED BEVERAGES	2.2-5.5
CIDER VINEGAR	about 3

* Actually these values are activities, or concentrations corrected for the attractive forces between ions of unlike charge in solution

Self Study Questions

1. What three classes of substances make up electrolytes? Give examples of each class.
2. What properties do electrolytes have in common?
3. Who first suggested that electrolytes must be dissociated in solution? How is our present conception of strong electrolytes different from that presented in the original ionization theory?

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4. What is meant when double arrows are used in writing an ionic equation? What is meant when one of these arrows is made stronger than the other?

5. Explain how equilibrium can exist in the ionization of acetic acid when nearly all of the material is in the form of the undissociated acetic acid molecules.

6. Under what conditions do ionic reactions go to completion? Illustrate each with an example. Give an example of an ionic reaction which reaches an equilibrium, rather than going to completion. Complete the equation:



7. What is an acid? What characteristic properties does it have?

8. How is hydrogen chloride prepared? What is the difference between this and hydrochloric acid? Write an equation to illustrate the change from one to the other, using the dot convention to show electron bonds.

9. Give several properties and uses of hydrochloric acid.

10. Describe briefly the preparation of sulfuric acid by the contact process. Include equations.

11. What are four properties of sulfuric acid which, together with its cheapness, make it such an important industrial chemical?

12. Mention several uses of sulfuric acid. If a liter of the acid (35% H_2SO_4 by weight) contains 441 grams of pure hydrogen sulfate, what must be the density of the solution? *Answer: 1.26 g./ml.*

13. Describe the preparation of nitric acid from ammonia. Include equations. What are the important properties and uses of this acid?

14. How is orthophosphoric acid prepared? Write the equation for the chemical change involved.

15. What is a base? What are the characteristic properties of bases?

16. How is sodium hydroxide prepared from common salt? What other important chemicals are formed during the process?

17. What substances are present in an aqueous solution of ammonia? Is this substance a strong or weak base? Write an equation showing the equilibrium which is reached when ammonia is dissolved in water.

18. Write formulas and electrovalences for the following ions: hydroxide, chloride, nitrate, sulfate, phosphate, carbonate, ammonium, calcium, sodium, potassium, aluminum, magnesium, silver, ferrous iron, ferric iron.

19. Reason out the formulas for the following electrolytes from the equal cation and anion valence rule: sodium carbonate, magnesium chloride, ferrous nitrate, ferric phosphate, aluminum sulfate, calcium hydroxide, carbonic acid, silver iodide, zinc fluoride.

20. Name several acids, bases, and salts, which are commonly found in the home. Which of these may be injurious? State the circumstances in each case.

21. What is meant by the term pH? Give examples of its use.

VIII

Solutions

Definition and Scope. The layman probably thinks of sugar or salt dissolved in water when the word *solution* is mentioned, but to the chemist the term means something much more general. Any substance forms a solution when its individual molecules, ions, or atoms disperse themselves throughout another substance haphazardly, rather than according to a definite pattern. Hence, in solutions a continuous variety of concentrations is possible. Sugar solutions can exist, for example, which contain anything from one sugar molecule to the tremendous number present in a saturated sugar solution. A solution differs from a pure substance in this respect, since the composition of the latter is constant for given isotopes of its constituent elements. Solutions are therefore merely special types of mixtures, differing from ordinary mixtures because they appear homogeneous to the eye, or even under high magnification, but still capable of being varied in composition like any other mixture.

A solution can be defined as a homogeneous mixture whose composition can be varied continuously¹ between certain fixed limits. The lower limit is the pure solvent containing no dissolved material, while the upper limit is the most concentrated solution that can be prepared. In some systems, particularly in certain liquid-liquid solutions, there is no upper limit, and the concentration of dissolved material can vary from zero to 100 per cent. Alcohol-water solutions fall in this category.

¹ Continuously in terms of human measurements, that is. The variation would be discontinuous to a molecular-sized being.



FIGURE 8 1 Solutions Concentrating sulfuric acid solutions Lead-lined valves, pipes, and tanks are employed Courtesy National Lead Company.

Under this definition a number of mixtures are seen to be solutions which are not commonly given the name. Air, for example, can be considered as a solution of oxygen, water vapor, argon, carbon dioxide, etc., in nitrogen. Likewise hydrogen gas can be thought of as dissolving in palladium, and carbon in iron,

to give solid solutions. Nine possible types of solution theoretically exist, based upon the states of matter, i.e., gases, liquids, and solids dissolved in gases, the same dissolved in liquids, and



FIGURE 8.2. Solutions. A dilute sulfuric acid-sodium bisulfate solution used in making cellulose rayon. Note the liquid viscose being forced through the many fine holes in the spinneret. It is chemically changed to cellulose in the bath and further on forms a rayon thread. Courtesy E. I. du Pont de Nemours & Company

the same dissolved in solids. However, liquids or solids molecularly dispersed in gases are considered as vapors rather than as liquids or solids.

Most of these types are of little importance to the beginning chemistry student as examples of solutions, and this discussion will be confined to only three: gases dissolved in liquids, liquids dissolved in liquids, and solids dissolved in liquids. In these systems the component present in smaller amount is called the *solute*, while the dissolving liquid is known as the *solvent*.

SOLUTIONS OF GASES IN LIQUIDS

Physical and Chemical Types of Solutions. In these solutions there is a variation in the affinity between the dissolved gas and the liquid. To consider the two extremes, the gas may have but little attraction for the liquid molecules, as we imagine is the case in a solution of nitrogen in water, or it may form strong chemical bonds, as when hydrogen chloride gas is dissolved in water. The first type is known as a physical solution and the second as a chemical solution. In the case of many, and probably all solutions, there is at least a weak attraction between the solute and the solvent, since otherwise the solute would not be expected to be soluble.

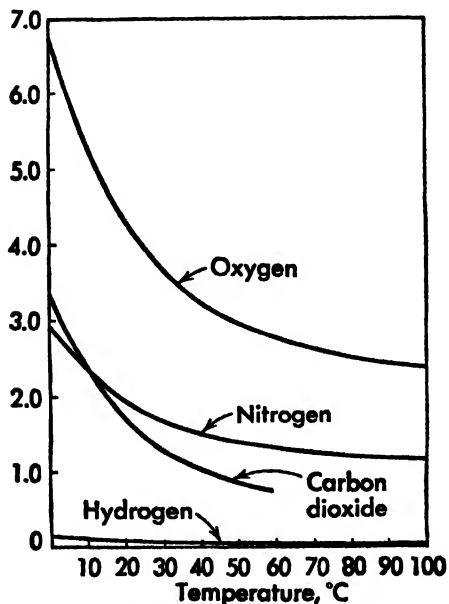
Properties of Physical Solutions of Gases in Liquids. All physical solutions of gases in liquids show the same general behaviour when gas pressure and temperature are altered. (a) The solubility of the gas varies directly with gas pressure, at constant temperature. (b) The solubility of the gas diminishes as the temperature of the system rises, at constant gas pressure. Let us consider these two effects in more detail.

Relationship between Gas Pressure and Solubility. The relationship between gas pressure and solubility is a direct proportion, and has come to be known as Henry's Law (William Henry, English chemist, 1803): *At constant temperature the weight of a gas which will dissolve in a given weight of liquid varies directly with the pressure of the gas upon the liquid.* Mathematically this becomes:

$$\frac{W_1}{W_2} = \frac{P_1}{P_2}$$

A familiar illustration of Henry's Law is the behaviour of a bottle of carbonated beverage upon being opened. Carbon dioxide is in solution in the beverage under pressure prior to removal of the bottle cap. When the cap is removed the pressure drops, the solubility of carbon dioxide diminishes, and the excess effervesces out. Another phenomenon due to Henry's Law is sometimes

noticed in tap water. As the latter warms up in the pipe it tends to lose its dissolved air; this, however, is kept in solution under pressure. When water is drawn from the tap the pressure drops



Solubility of carbon dioxide (grams per liter) and of oxygen, nitrogen, and hydrogen (grams per 100 liters) in water at various temperatures.

FIGURE 8.3. Solubility of Common Gases in Water Pressure of dry gas constant at 760 mm.

and the excess air comes out of solution at once as many tiny bubbles which slowly rise to the surface.

Supplementary problems involving Henry's Law are given in Chapter XXVI.

Effect of Temperature upon Gas Solubility. The effect of temperature upon gas solubility cannot be formulated mathematically, at least not with simple mathematics. But there is a general effect, namely that the solubility of a gas in a liquid diminishes as the temperature rises. The solubility change under these conditions is opposite to that of most solids dissolved in liquids. An example of this temperature effect often seen in the home is the appearance of air bubbles, sometimes mistaken for steam, when a container of water is heated. Since these bubbles appear far below the boiling point they are not steam,

but excess air coming out because of the lowered solubility of oxygen and nitrogen at the higher temperature. The solubilities of some common gases in water at different temperatures is given in Figure 8.3.

SOLUTIONS OF LIQUIDS IN LIQUIDS

Liquid-liquid solutions tend to behave in an unpredictable manner when pressure and temperature are changed, hence it is not possible to make general statements of the type given on the last few pages. However, a rough prediction of solubility can sometimes be made, based upon the general rule that substances made up of similar molecules, or molecules with similar groups, tend to be soluble in each other. For example, all hydrocarbons (compounds of carbon and hydrogen) are mutually soluble, as shown by the product petroleum, which is chiefly a mixture of a large number of hydrocarbons dissolved in each other. Also alcohol and water, both with molecules containing the —OH group, are miscible liquids.

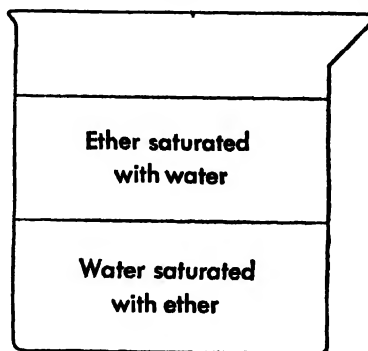
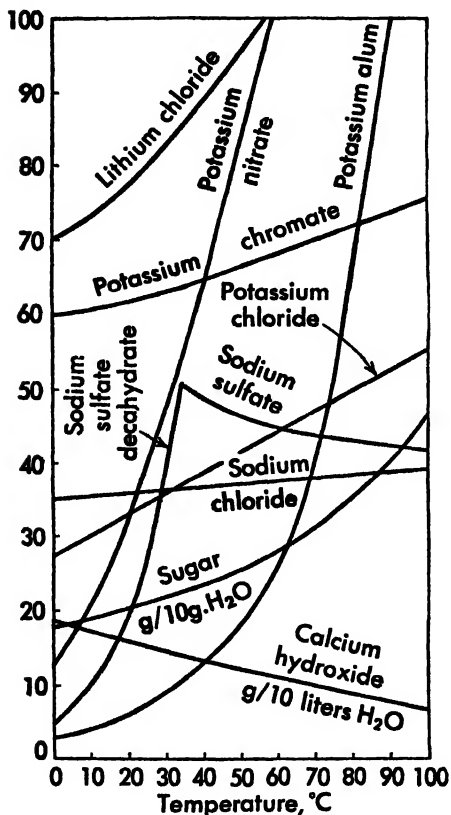


FIGURE 8.4. Partial Miscibility
Neither liquid phase is pure,
since both are saturated solutions

Two liquids may be virtually insoluble in each other, as water and lubricating oil. We say they are *immiscible* liquids. Others are soluble in each other in all proportions, as water and alcohol. These we call *completely miscible*, or miscible in all proportions. Some liquids are *partially miscible*, which means they dissolve in each other to a limited extent. Ether and water make such a pair. When these liquids are shaken together in approximately equal amounts two layers are formed. The upper layer is ether saturated with water (containing about 2 per cent water) and the lower layer is water saturated with ether (containing about 6 per cent ether).

SOLUTIONS OF SOLIDS IN LIQUIDS

Effect of Temperature. Solutions consisting of solids dissolved in liquids probably comprise the most important class of solutions. Most solids increase in solubility as the temperature of



Solubility of various solids in grams per 100 grams water, except sugar (grams per 10 grams water) and calcium hydroxide (grams per ten liters)

FIGURE 8.5. Solubility of Various Solids in Water at Different Temperatures.

the system is raised, as shown by the solubility curves in Figure 8.5. Note, too, that the solubility of most solids in water increases with temperature at a faster rate than that of salt. There are also a few exceptions, such as calcium hydroxide and calcium sulfate, which decrease in solubility with rising temperature. The experimental determination of solubility sometimes leads to curves of the type shown by sodium sulfate (Figure 8.5). The discontinuity is due to the fact that the solubility of two sub-

stances is being shown, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Na_2SO_4 . The hydrate is not stable above 32.4°C ., and above that temperature the solubility curve is that of the anhydrous salt.

Terminology. Various terms are used in describing solutions, and while these apply chiefly to solutions of solids in liquids, they may also be employed in connection with gas-liquid and liquid-liquid systems. The solid is called the *solute*, and the liquid 'the *solvent*. Solutions are called *concentrated* or *dilute*, based upon whether much or little solute is present, e.g., a 35 per cent hydrochloric acid solution would be concentrated, while a 2 per cent sodium hydroxide solution would be dilute. Depending upon the degree of saturation, solutions may also be *unsaturated*, *saturated*, or *supersaturated*. These terms need careful defining.

Degrees of Saturation. A solution containing less solute than required for saturation at a given temperature is called *unsaturated*. If excess solute is added to a solvent and is dissolved to the maximum extent possible *at constant temperature*, and in the absence of evaporation, a *saturated* solution will be formed. The chemist prefers to define a saturated solution in terms of solution and deposition rates. When excess solute stands in contact with a solvent at constant temperature, solution and deposition continually take place in a dynamic process not apparent to the eye. At first the rate of solution is much faster than the rate of deposition. As more solute dissolves the two rates become more nearly the same, and eventually become equal at saturation. *A saturated solution, then, is one in which the dissolved solute is in equilibrium with the undissolved solute*, meaning the rate of deposition is the same as the rate of solution. Even after saturation is reached the dissolving and the deposition continue, as evidenced by a gradual change in the size and shape of the remaining solute crystals.

A solution does not necessarily have to contain much solute, i.e., be concentrated, in order to be saturated. A sparingly soluble substance may form a saturated solution which is quite dilute. A liter of saturated barium sulfate solution at room temperature, for example, contains only about 0.002 gram of this salt.

If a clean, saturated solution is carefully cooled, it may retain all of its solute at the lower temperature. It will then have more solute dissolved in it than the saturation amount for that lower temperature. Such solutions are called *supersaturated*. They exist in an unstable condition because of the absence of favorable surfaces for growth of crystals. If a crystal of the solid solute is added to a supersaturated solution, the excess solute quickly deposits upon this, and a normally saturated solution remains.

Three solutions of a substance, one unsaturated, one saturated, and one supersaturated, can be distinguished by dropping a crystal of the solute into each container. The crystal in the unsaturated solution will dissolve, at least in part. The crystal in the saturated solution will remain unchanged in mass as long as the temperature is kept constant and evaporation of the solution is prevented. The crystal in the supersaturated solution will grow in size, and if the degree of supersaturation is high a considerable amount of solid solute may form.

Methods of Expressing Concentration. The concentration of a solution can be expressed as grams of solute per 100 grams of solvent, as in the graph in Figure 8.5. A common method also is to describe the strength of a solution by giving the number of mols² of solute present per liter of *solution*. This is called the *molarity* of a solution. Thus, 58.5 grams of sodium chloride dissolved in enough water to make a liter of solution gives a one-molar solution, since the liter contains one mol of sodium chloride. If 5.85 grams were present it would be a tenth-molar solution, and if 7.02 grams were dissolved a 0.120-molar solution would result. Since molecular weights vary widely, solutions of the same molarity may have very different weights of solute present per liter of solution. For example, a one-molar solution of table sugar ($C_{12}H_{22}O_{11}$) would contain 342 grams of this substance per liter, while a molar solution of formaldehyde ($HCHO$) would contain only 30 grams of solute per liter.

² The term mol is used here to mean gram molecular weight.

Normality. Another method of expressing electrolyte concentration is used by chemists in which solutions of equal reacting power have their strengths shown by the same numerical values. This is not accomplished by using grams of solute per 100 grams

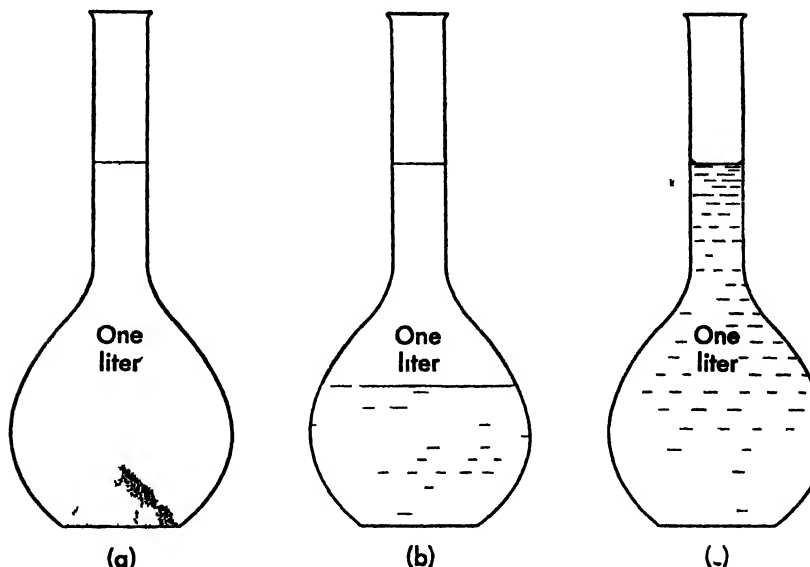


FIGURE 8.6 Preparation of a Normal Solution (a) A gram equivalent weight of electrolyte is weighed into a volumetric flask (b) The substance is dissolved. (c) The solution is diluted to a volume of one liter

of solvent, since electrolytes do not in general react on an equal weight basis. (56 grams of KOH reacts with 36.5 grams of HCl, for example.) Nor is the use of molarity satisfactory, because, while some electrolytes react mol for mol, many others do not. (One mol of $\text{Ba}(\text{OH})_2$ reacts with two mols of HCl, for example.)

If, instead of the mol, another unit is utilized which is the mol divided by the number of hydrogen atoms in the formula which dissociate (for an acid), or the number of hydroxide groups (for a base), or the total anion or cation valence (for a salt), then the number of these new units per liter of *solution* will be a measure of reacting strength. This method of expressing concentrations is in wide use, and the numerical values employed are known as *normalities*. The unit obtained as described above, by

dividing the gram molecular weight of an electrolyte by a small whole number, is known as the *gram equivalent weight*, or often simply as the *equivalent* of a substance.

Thus, hydrogen sulfate, H_2SO_4 , the solute in sulfuric acid, has a gram equivalent weight of $98/2$, or 49 grams. The small whole number in this case is two because two hydrogen atoms ionize and dissociate from a molecule of hydrogen sulfate when it is dissolved. An equivalent of sodium hydroxide is the same as a mol, the small whole number being one because of the one hydroxide ion which dissociates. The gram equivalent weight of aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, is $342/6$, or 57 grams. (Why?)

A solution containing an equivalent of any electrolyte per liter hence has a normality of one. If two such electrolytes react, equal volumes of one-normal solutions will be required for a complete reaction. The normality of the solution need not be one, of course. It can be any value up to a maximum representing the most concentrated solution that can be prepared. As a general definition, then, *normality is the number of gram equivalent weights of electrolyte dissolved in a liter of solution*. Supplementary problems in normality are given in Chapter XXVI.

Important Solutions. Solutions of importance in which water is the solvent include all natural waters, since these contain dissolved air and salts, and all fluids associated with living plants and animals, e.g., blood, perspiration, plant juices, etc. Ink is a water solution of colored substances, or of chemicals which form colored precipitates in the presence of air. Many important solutions exist involving compounds of carbon (organic compounds), such as petroleum and coal tar. Varnishes and enamels are in part solutions of resinous substances in organic solvents. Lubricating oil is a complex mixture of many hydrocarbons dissolved in each other.

Liquid air is chiefly a solution of oxygen in nitrogen. Many metal alloys are solutions of one metal in another, as the mixture of copper and zinc which we call brass, or the amalgams, which are other metals dissolved in mercury. Fused salts often dissolve

in one another, as the mixture of magnesium chloride, sodium chloride, and calcium chloride used in the electrolytic preparation of metallic magnesium.

Self Study Questions

1. Give a general definition for the term solution.
2. Name five solutions commonly used in the home.
3. What types of solutions are possible based upon the states of matter? Of these, which are the most frequently encountered?
4. What two factors affect the solubility of gases in liquids in the case of physical solutions? Give examples in the home where gas solubility is influenced by these factors.
5. State Henry's Law. If 0.753 gram of gas dissolves in a liter of water at 20°C . when the gas exerts a pressure of 760 mm., what weight of gas will dissolve at 20°C . when its pressure is three atmospheres?
6. Give examples of immiscible, partially miscible, and completely miscible liquid pairs. In partially miscible pairs which have been standing in contact for some time are the two phases pure liquids? Explain.
7. What is the effect of temperature upon the solubility of most solids in liquids? Give an exception to this general trend.
8. Distinguish between a supersaturated, saturated, and unsaturated solution. How could you tell in the laboratory in which category a particular solution happened to be?
9. Name three ways in which the concentrations of electrolyte solutions can be expressed. From the graph on page 174, what will be the solubility of potassium alum (page 234) in grams per 100 grams of water, at 50°C .?
10. What is a molar solution? What is the general meaning of the term molarity? What will be the molarity of a solution which contains 20.6 grams of sodium chloride per liter? *Answer: 0.35 Molar.*
11. What is a normal solution? Give the meaning of the general term normality. What is the normality of a H_3PO_4 solution which contains 35 grams of this substance per liter? *Answer: 1.07 Normal.*
12. What is meant by the gram equivalent weight of an acid, base, or salt? From the table of electrovalences on page 162, find the electrolyte (a) with the largest equivalent weight, (b) with the smallest equivalent weight.

PART THREE

Inorganic Components of the Solid Earth

IX

Silica and the Silicates

The crust of the earth is very largely made up of compounds of the element silicon in which the latter is combined with oxygen, or with oxygen and the various metals. These compounds, taken together, comprise nearly 90 per cent of the solid surface of the earth, and the study of their composition and physical properties such as appearance, crystal form, hardness, and streak¹ constitutes a large part of the science of mineralogy. There are also a number of silicate products made by man, such as glass, pottery, and cement, manufactured in the important ceramic industries. Some of the more familiar of these natural and synthetic silicates will now be discussed.

SILICON DIOXIDE

Occurrence. The element silicon does not exist in nature in the free state. The simplest of the naturally occurring silicon compounds is the dioxide, SiO_2 . This goes under the general name of *silica*, and is also given other names. In the form of pure hexagonal crystals it is known as *quartz*; these are common in nature and in some instances have grown so large that they weigh hundreds of pounds. Quartz may be colored or made opaque with impurities. Examples are *amethyst*, a purple or bluish-violet quartz colored with manganese compounds, and *milky quartz*, containing air bubbles. Chalcedony, flint, jasper, and opal are other impure forms of silicon dioxide. Large silica

¹ The color of the fine powder of a mineral, obtained by rubbing against a hard white surface. It is often an important distinguishing property.



FIGURE 9.1. A Specimen of Quartz. Courtesy Ward's Natural Science Establishment, Inc.

deposits have been formed in the geological past from the accumulation of vast numbers of skeletons of tiny marine organisms known as diatoms. In most animals the shells or bony parts are largely calcium carbonate or phosphate, but the diatom utilizes silica for this purpose. This form of silica, known as diatomaceous earth, is used as an absorbent and in scouring powders. Silicon dioxide is also one of the components present in certain complex rocks, such as granite. Sand, particularly if it is light in color, is chiefly silica. Some plants (bamboo, rushes) and some animal parts (bird feathers, sponge spicules) have a higher than usual silica content.

Structure of Quartz. The crystal structure of silica reminds one somewhat of that of ice (page 121). Each silicon atom is attached by covalent bonds to four oxygen atoms, as shown in Figure 9.2, just as each oxygen atom in ice is attached to four hydrogen atoms. However, the silicon-oxygen bond is much stronger than the hydrogen-oxygen linkage in ice.

Fused Quartz. When quartz is heated it changes to the allotropic forms tridymite (870°) and cristobalite (1450°) and then begins to soften above 1700°C. When it is soft it can be shaped. The cooled material is a glass-like substance known as fused quartz. Articles made from this have several advantages. They undergo very little change in volume with change in temperature. Fused quartz therefore remains largely free from strain even though suddenly heated or chilled over a considerable temperature range, this behaviour being quite different from that of crystalline quartz. Thus, a quartz dish can be heated to redness and plunged into cold water without shattering. Fused quartz is also chemically inert, being attacked by only a few reagents (chiefly alkalis and hydrofluoric acid). A further advantage of fused quartz lies in its high transparency to ultraviolet light, it being much better than ordinary window glass in this respect.

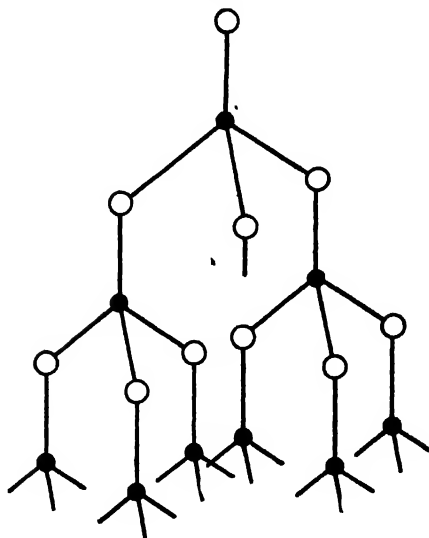
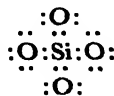


FIGURE 9.2. Crystal Structure of Quartz. Each silicon atom (black disk) is joined to four oxygen atoms (circles) by a pair of shared electrons (lines).

1. NATURALLY OCCURRING SILICATES

By far the greater part of the silicon found in the earth's surface is present in combination with oxygen and various metals, in the naturally occurring silicates which make up most of our rocks and minerals. The fundamental building unit in all of these silicates is the SiO_4^{4-} tetrahedron² (Figure 9.3), with four

² As shown at the right, the five atoms in this tetrahedron have a total of 32 outer electrons, shared and unshared. This accounts for the ion charge of negative four, since four neutral oxygen atoms and one neutral silicon atom have only $(24 + 4)$ or 28 outer electrons.



oxygen atoms at the corners and a silicon atom in the center. In addition these minerals contain the proper number of positive

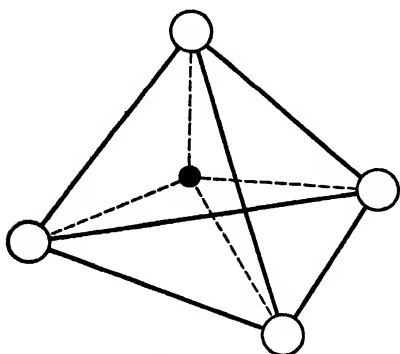
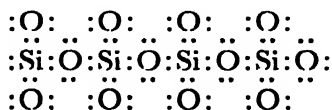


FIGURE 9.3. The SiO_4 ----- Tetrahedron. Oxygen atoms are at the corners and a silicon atom is in the center.

metal ions to balance the negative charge and produce a neutral crystal. The commonest metal ions present are those of aluminum, iron, calcium, magnesium, sodium, and potassium. Hundreds of naturally occurring silicate minerals are known, many with complicated formulas. These are so numerous and complex for three reasons.

First, two or more SiO_4 ----- tetrahedra may share a corner (an oxygen atom, that is) producing combinations like Si_2O_7 -----, as in the mineral *serpentine*, $\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. The sharing of oxygen atoms may result in continuous filaments or sheets of oxygen and silicon atoms. Thus the mineral asbestos has very long chains made up as shown below. It is seen that this chain is a reproduction of the SiO_3 --- ion. In the mineral asbestos the extension is so great that the chain may contain many millions of atoms.



The chain can be considered as $(\text{SiO}_3)^{--})_x$, although there are no discrete SiO_3^{--} ions present as such. There must be metal ions present with the necessary positive charge to insure a neutral crystal. In asbestos these are magnesium and calcium ions, present between the silicate filaments. The formula for asbestos could be most correctly shown by writing $\text{Mg}_{3x}\text{Ca}_x(\text{SiO}_3)_{4x}$, where x is somewhat variable but with values of many millions. However, this is simplified for convenience (as in the case of many solids) to $\text{Mg}_3\text{Ca}(\text{SiO}_3)_4$. The long silicate chains account for the peculiar, filament-shaped asbestos crystals. The silicate

tetrahedra may also be arranged in continuous *sheets* of silicon and oxygen atoms in which all of the oxygens are shared, except at the edges of the crystal, leading to a giant ion which is a continuous reproduction of an $\text{Si}_4\text{O}_{10}^{--}$ unit. This accounts for the ready cleavage of minerals like mica and talc. The metal atoms in such crystals are between

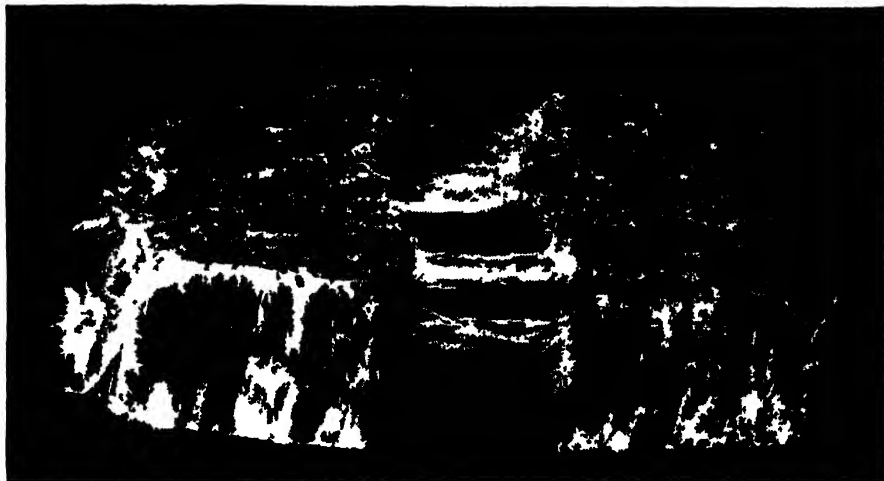


FIGURE 9.4. Asbestos, an Unusual Silicate Mineral. Courtesy Ward's Natural Science Establishment, Inc.

the sheets. Besides filaments and sheets, various three-dimensional silicon-oxygen structures are possible, the commonest one being that found in ordinary quartz. In the latter substance no extra electrons are necessary to satisfy the rule of eight. No negative silicate ions are formed, hence no metal ions are needed to produce neutral crystals.

Second, the great variety of silicate minerals is caused in part by the fact that several kinds of metal atoms may be present in a given mineral, replacing each other in a random manner. Usually the valence of a replacing ion is the same as that of the metal ion being replaced, but even this is not always the case. The mineral augite, as an example, is calcium magnesium aluminum iron silicate, with an indefinite amount of each metal, the only limitation being that the total positive charge on the metal ions must be equal to the total negative charge due to the silicate ions.

Third, the elements aluminum and beryllium sometimes replace the central silicon atoms in the silicate tetrahedra. This alters the charge on the silicate ion, because aluminum and beryllium have three and two outer electrons as compared to silicon's four. Thus, when one Si atom in a group of four neutral SiO_2 units (in the interior of a crystal) is replaced by an aluminum atom, the group AlSi_3O_8 which is formed has one negative charge.³ A three-dimensional network built from such units must therefore have compensating positive ions. An example of such a silicate is the common orthoclase feldspar, where the metal ion is univalent potassium ($\text{K}^+\text{AlSi}_3\text{O}_8^-$).

S O I L

While the crust of the earth, considered at some depth, consists chiefly of silicate minerals, the surface portion which is able to support plant life is more complex than this. It contains, besides such weathered silicon or carbonate minerals as sand, clay, or limestone, a significant amount of an indefinite substance known as *humus*, and also much living matter, as plant roots, worms, and a host of different kinds of microorganisms.

Humus is the residual part of leaves, roots, or wood left after rotting of these plant structures has taken place. It is largely made up of giant organic molecules of uncertain composition, but consists in part of cellulose. While humus is generally regarded as being chemically rather inert, it perhaps aids in solubilizing mineral matter in the presence of water so that important inorganic ions, needed by the plant for growth, are available in greater numbers when it is present. Humus also makes soil porous, permitting air and water to penetrate to plant roots, and it absorbs these, particularly the water, so that the soil can retain the latter during periods of dry weather. Humus likewise furnishes a favorable environment for necessary bacterial growth.

³ One extra outer electron, besides those present in the neutral atoms, is needed to satisfy the rule of eight, since the aluminum ion has one less outer electron than the silicon atom which it replaces.

GLASS

Physical Nature of Glass. Man takes advantage of the transparency and water insolubility of certain silicate mixtures which are not too difficult to fuse and shape, in a group of



FIGURE 95 Early Glassware German beakers with enamel, about 1600. Courtesy of the Cleveland Museum of Art Gift of Mrs Henry White Cannon

substances known as *glasses*. These mixtures have the important property, when correctly made, of remaining largely amorphous (not crystalline) when cold. The solid glasses thus have an un-oriented, random arrangement of their ions which approaches that characteristic of the liquid state. This is an advantage because it increases their transparency, i.e., light would pass less readily through a mass of closely packed crystals. A truly amorphous glass also does not polarize light, or cause double refraction phenomena.

Glass has been made and used for a very long time. The Egyptians employed it about seven thousand years ago. The earliest use of glass probably occurred long before that, however, when

the first savage made a spearhead or an ornament out of obsidian, a volcanic glass found in nature. While glass is an antique substance, modern research has evolved forms and uses for it which are entirely different from anything known to the ancients.

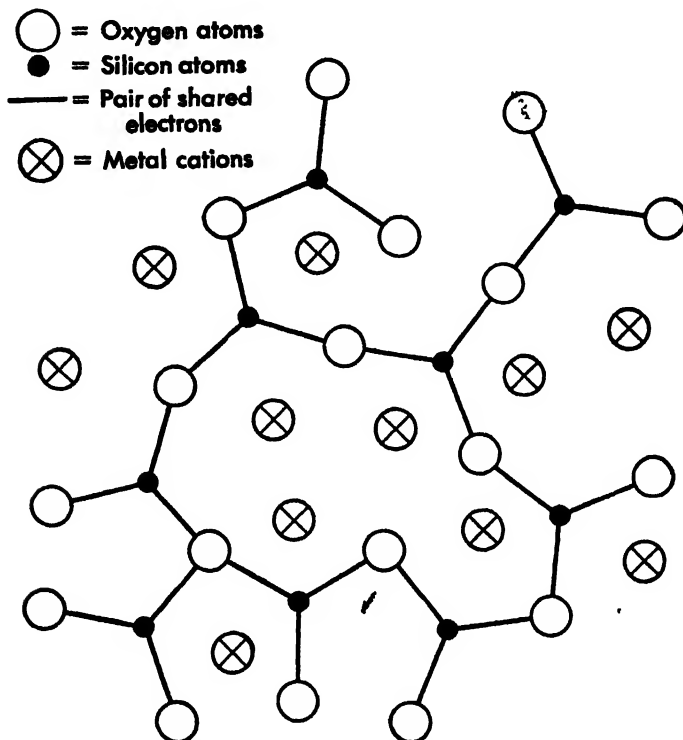


FIGURE 9.6. Glass. The diagram shows the complex silicate anions and metal cations present in this substance.

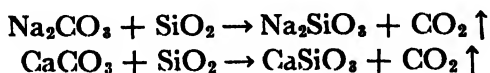
The commonest glass, used in windows, bottles, dishes, etc., is soft, or soda glass. It is a mixture of sodium and calcium silicates usually containing in addition small amounts of magnesium, potassium, aluminum, and iron silicates. If the metal silicates are considered to have the formulas Na_2SiO_3 and CaSiO_3 , then glass also contains an excess of silica.⁴ Common glass is usually made by heating sand (SiO_2) with soda ash (Na_2CO_3) and lime-

⁴ Actually, instead of SiO_3^{--} ions and SiO_2 molecules, complex silicate anions of the types described on page 187 are present. This structure is indicated in Figure 9.6.



FIGURE 9.7. Mixing a Batch for Manufacture of a Special Glass. Materials weighed into mixer at left, then loaded into cars for transport to melting furnaces. Courtesy Libby-Owens-Ford Glass Company.

stone (CaCO_3). The silica displaces carbon dioxide as the temperature is elevated, causing the carbonates to be converted to silicates.



These reactions take place in a furnace. The mixture effervesces as carbon dioxide comes off, then settles to a quiet liquid. However, the formation of a tank of molten glass is only the beginning of the process of glass making, and considerable skill is still required to create the familiar glass objects seen on every hand.

✓**Glass Working.** In days gone by glass objects were made by artisans who required much training to become proficient at the work, but today most common glass articles are made mechanically. Most window glass is now extruded between rollers as a wide ribbon; bottles, electric lamp bulbs, etc., are rapidly blown

in machines which use compressed air; glass fibers are made by forcing molten glass, at a high rate of speed, through tiny openings having one-quarter the diameter of a human hair or less. Some glass objects are still made by hand, rather than mass produced, because of their unusual shape or size. After glass objects are formed they must go through a period of slow cooling, known as *annealing*, to prevent the cold object from being under a condition of strain which would cause it to crack under slight shock or temperature change. Strain in glass can be detected by examining it under polarized⁵ light.

Other Types of Glass. Many other kinds of glass are now used besides soft glass. *Pyrex* glass is chiefly a mixture of silicon dioxide and boric oxide, with small amounts of sodium and aluminum oxides, and smaller amounts of other metal oxides. It can be regarded as a sodium aluminum borosilicate. It is more resistant to chemicals than ordinary glass, and expands less when heated, so that it is better able to withstand sudden temperature changes. *Lead* or *flint* glass is a lead potassium silicate, soft, but with a high index of refraction, and hence possessing the "sparkle" that is desirable in artificial jewels and cut glass. This glass is also used in making light bulbs and neon sign tubing. *Hard* glass is a product in which potassium has been substituted for the sodium in common or soft glass. *Optical* glass is a complex mixture of silicates used for lenses.

✓ **Colored Glass.** Glass is colored by the presence of impurities, or by the purposeful addition of small amounts of coloring agents. Common glass often appears green when viewed through a considerable thickness. This is due to a small amount of ferrous silicate present as an impurity. It can be corrected by the addition of a little manganese dioxide. Large amounts of the latter substance, on the other hand, give a black glass. The blue color sometimes imparted to glass is produced by addition of cobalt compounds. Selenium and its oxide give an orange or red glass,

⁵ See page 369.

as does gold. A yellow glass also results from addition of cadmium sulfide. White, opaque glasses are made by adding insoluble, finely divided substances, such as calcium fluoride, stannic oxide, or calcium phosphate.



FIGURE 9-8 Research in Glass. Small laboratory furnaces are used for melting experimental mixtures like the one shown. Courtesy Libby Owens Ford Glass Company

Modern Uses for Glass. In this modern age glass is used in many new and different ways. It is forced through tiny openings to make *glass fibers*, and the latter can be woven into cloth or made into masses of material suitable for use as a filter, or as an insulating material. Glass is bonded to plastic sheets, giving *safety glass*. The latter consists of three layers, the two outer ones being glass and the inner one being a flexible vinylite plastic. Such glasses do not shatter under impact, as everyone knows, because the plastic layer “gives,” but does not break into pieces, so that it holds the glass fragments to it. *Wire glass* is a product containing wire imbedded in the glass. It does not break easily,

and the wire prevents a rapid falling away of the softened glass in case of fire. *Invisible glass*, used in some showcases and windows, has on its surface a film of metallic fluorides or other compounds



FIGURE 9.9. Safety Glass. Curved windshields ready for lamination are placed in the steel tub which later becomes a part of the autoclave in which they are given heat and pressure treatment by means of oil, after which the glass-plastic sandwich becomes a single, transparent unit. Courtesy Libby-Owens-Ford Glass Company.

which cause a marked decrease in the amount of reflected light, to a value of less than half of one per cent of the incident light. *Tempered glass* is a product made by rapid cooling of the surface with air. It is stronger and more flexible than ordinary glass, and when it does break it crumbles rather than shattering. Another modern glass, *Vycor*, made by dissolving out the metallic components with acid, approaches fused quartz in composition and properties (Figure 9.10). *Glass bricks* are used in building construction. They have the twofold advantage of admitting light and being good insulators. A transparent glass with a sur-

face which *conducts electricity* is now made. Its surface can be electrically heated, making it of value in windows and windshields, since icing and fogging can be prevented. The conducting layer is a thin film of metallic oxides.

CERAMICS

The ceramic industries include all man-made silicate products, e.g., glass, cement, pottery, etc. But an older and still widely used definition limits ceramic products to those made by heating clay, such as bricks, tile, pottery, and porcelain. Articles of this type have long been made by man, as the reader knows from visits to museum exhibits of ancient pottery and china.

Clay is a secondary product resulting in nature from the weathering of feldspar. Carbon dioxide and water react slowly upon the latter throughout geological periods of time to produce the mineral *kaolinite* ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), a white, finely divided substance when pure. While kaolinite is the chief component of clay, the latter is usually colored because of the presence of impurities.

Clay or kaolinite has the unusual property, different from most other minerals, of being highly water absorbent, and of forming with water plastic masses which can be shaped into useful articles. Certain clays, i.e., ceramic or potter's clay, can be dried and sunbaked or kiln-baked, after being so shaped, without losing their form or undergoing significant cracking. Some shrinkage takes place (about 10 per cent with many kiln-baked



FIGURE 9.10. Vycor Glass. This material, made by dissolving the metallic components from glass, approaches fused quartz in its composition and properties. In the test molten metal is being poured into the container which sets on ice, without causing it to crack. Courtesy Corning Glass Works.

objects), but the dried or baked clay then forms a coherent, fairly hard product, suitable for pipe, brick, containers, etc.



FIGURE 9.11. Early Ceramic Ware. Greek Amphora, VI Century B.C. The A. W. Ellenberger Collection. Courtesy the Cleveland Museum of Art.

The crudest ceramic objects, such as porous tile or brick, are made in this way, by shaping moist clay and heating it. In the firing process the light green ferrous compounds in the clay are converted to reddish-brown ferric compounds, accounting for the familiar color of these objects. The temperature of firing is usually not high enough to fuse the objects being baked; however, a temperature sufficient to cause partial fusion is sometimes employed, giving products such as vitrified brick.

White Pottery. A purer clay is used for ceramic products like porcelain or chinaware (white pottery). This is mixed with other ingredients, feldspar and silica being common. The shaped articles are fired to give unglazed, porous products known as biscuits or bisques. They must then be treated further, to give them a shiny, impervious surface, in a process known as *glazing*. The cheapest glaze, used on sewer pipe, tile, etc., is produced by adding salt to the surface of the hot objects. This reacts with the clay to give a fusible product—largely sodium aluminum silicate—which melts and coats the article. More durable glazes, better able to stand temperature changes and abrasion, are made with complex silicate mixtures which may also contain borates. These are applied in the form of a paste to the surface of the bisque and the whole is reheated to a temperature which will cause the glaze to fuse and fill the surface pores of the bisque, but not hot enough to melt the bisque. Upon cooling, the article has the familiar shiny surface seen so commonly on dishes.

It is highly important that the glaze expand or contract with rise or fall in temperature to the same extent as the bisque. Otherwise the glaze cracks, and the reader will undoubtedly recall seeing dishes in which the glaze is full of intersecting cracks caused by unequal expansion of the two parts.

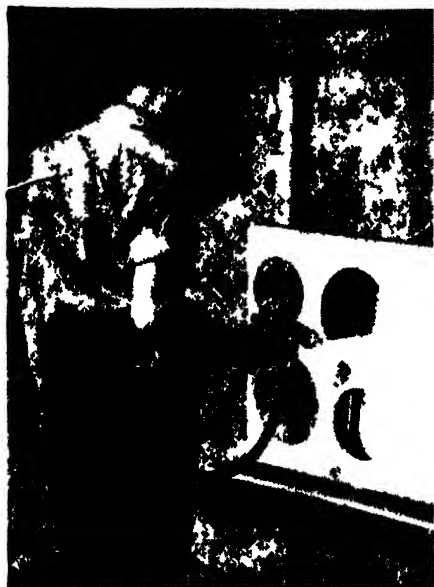
The decoration on ceramic articles can be applied either under or over the glaze (underglazing, overglazing). In the former it is applied to the bisque, and usually consists of a mixture of metallic oxides. In the latter it is applied to the glaze, and consists usually of silicates.

Vitreous Enamels. When silicate mixtures are fused to metal they are called vitreous enamels, or simply enamels. To make these mixtures silica and feldspar and insoluble opacifiers, such as titanium oxide or calcium fluoride, are melted and quenched in water. The product, called a frit, is finely ground, made into a paste, applied to the metal surface, and fused on. Enamelled articles of this type are in everyday use in the form of bathtubs, sinks, refrigerators, tables, saucepans, and stoves. Care must be taken here, as with glazed pottery, to have an enamel with the same coefficient of thermal expansion as that of the underlying metal

PORTLAND CEMENT

Portland cement⁶ is another important silicate product. It is mixed with sand, coarse aggregate, and water to make concrete. Concrete is used in the construction of highways, airport runways, sidewalks, bridges, dams, large buildings, and a multitude of other major and minor projects. Steel rods or wire may be incorporated in the mass to make reinforced concrete. A large amount of cement is used in all parts of the world for construction purposes. In the United States the production of portland cement in 1950 was about 220 million barrels, each barrel containing 376 pounds.

⁶ Named because of its resemblance to a building stone quarried near Portland, England.



(a)

Manufacture of Cement.

A wide variety of calcareous (calcium carbonate as in limestone) and argillaceous (aluminum silicate as in clay) materials are used in making portland cement. These are finely pulverized, intimately mixed, and then calcined in large rotary kilns at a temperature of about 1500°C . to form clinker. In the calcining process the calcium carbonate in the raw materials combines with the silica and aluminum oxide to form cal-



(b)

FIGURE 9.12. Manufacture of Enamelware (a) Spraying the final or cover coat of porcelain enamel on range tops (b) The firing operation. Furnace is at left and is U-shaped. Articles go in at right opening and come out at left. Courtesy Ferro Corporation.

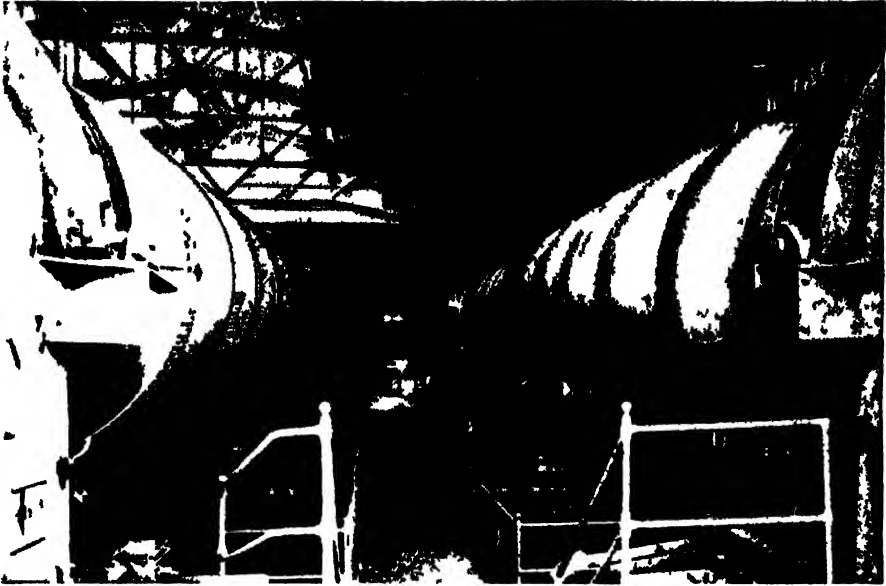
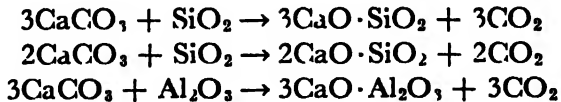


FIGURE 9 13. Rotary Kilns used in Cement Manufacture. Courtesy Portland Cement Association

cium aluminates and calcium silicates in reactions such as the following:



The clinker contains about 80 per cent of calcium silicates and 20 per cent calcium aluminates. The clinker, along with a small amount of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), is ground to a fine powder to form portland cement. The gypsum is added to regulate the rate of initial hardening.

Setting of Cement. When portland cement is mixed with water chemical reactions of hydration and hydrolysis occur which cause the mass to set and harden. Hydration of calcium aluminates causes the initial hardening.

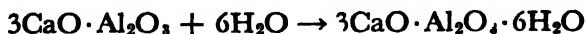
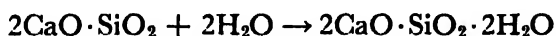




FIGURE 9.14. Cement Manufacture. The hot clinker from the kiln is cooled before further treatment. Courtesy Portland Cement Association.

The greater part of the strength is obtained from the hydration of calcium silicates, however, as for example:



These reactions occur slowly and continue for a long time with the result that portland cement concrete continues to gain strength for many years. Concrete remains plastic for an hour or longer which permits it to be placed in desirable shapes or forms. It then hardens rapidly so that forms may be removed and reused for further construction.

Prestressed Concrete. A recent advance in the field of reinforced concrete is *prestressed concrete*, in which the tensile strength is increased by putting the reinforcing metal under tension. When this is done it is possible to use longer spans of concrete, with fewer supports and less arching.



FIGURE 9.15. An Illustration of the Use of Cement. Grand Coulee Dam. Courtesy Portland Cement Association.

Self Study Questions

1. Name several varieties of silicon dioxide which occur in nature. Are they all pure silica?
2. What changes take place when quartz is heated? What are the advantages of articles made from fused quartz?
3. What is the basic silicon-oxygen structure present in all silicate minerals? Account for the ion charge of -4 which this unit possesses.
4. Calculate the ion charge of the Si_3O_{10} ion in which three SiO_4 tetrahedra share two oxygen atoms. (Footnote, page 185.)
5. Give three reasons why there are such a variety of silicate minerals found in nature. Illustrate these with examples.
6. How does soil differ in composition from the earth's crust at a depth of, say, 500 feet?
7. What are the common starting substances used in making soda glass? Write equations for the reactions which take place when these are heated.
8. How do Pyrex glass and lead glass differ in properties and in composition from soda glass?
9. Look up the etymology of the word "ceramic."
10. Describe the operations necessary for making a piece of white pottery, such as a dish.
11. How is vitreous enamel prepared and put on metal? What precautions are taken to insure that glazed pottery or vitreous enamelled objects can withstand moderate temperature changes?
12. What two chief ingredients are used in the manufacture of portland cement? What reactions are thought to take place when these are heated together?
13. What additional substance is added during the grinding of cement clinkers? What is its purpose?
14. Write equations for chemical changes that are thought to take place during the setting of cement.
15. Distinguish between cement and concrete.

X

Three Important Nonmetals

While the earth's crust is chiefly silica and metallic silicates, other important substances are also present. Metallic compounds containing one or more of the elements oxygen, chlorine, phosphorus, sulfur, and carbon occur in significant amounts. Valuable deposits of uncombined sulfur and carbon are also found. The chemistry of oxygen and chlorine has already been mentioned, and some familiar metals will be discussed in the next chapter. Let us now consider briefly the three remaining elements carbon, sulfur, and phosphorus, and some of their naturally occurring compounds in the earth's crust. These three elements are nonmetals, since they do not in general have the malleability, ductility, luster, heat conductance, electrical conductance, or the small number of outer electrons per atom which characterize the metals.

✓ CARBON

Occurrence. The element carbon is present in both the free and combined states in nature. It is found free in two crystalline varieties, *graphite* and *diamond*, and as a number of other, less pure forms. It occurs combined in the gas carbon dioxide, already mentioned, and in much larger amounts as various metallic carbonates, of which calcium carbonate is the most common. Carbon is also the key element in a number of substances and mixtures associated with life, past or present, which will be discussed later, as coal, petroleum, hydrocarbons, cellulose, sugar, rubber, etc.

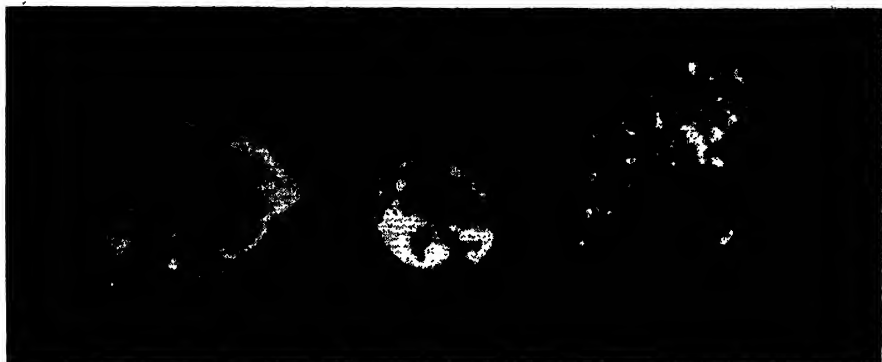
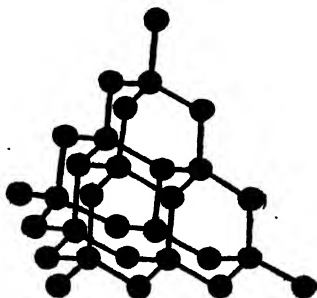


FIGURE 10.1. Forms of Carbon. Left to right, graphite, diamond, coal. Courtesy National Carbon Division, Union Carbide and Carbon Corporation.

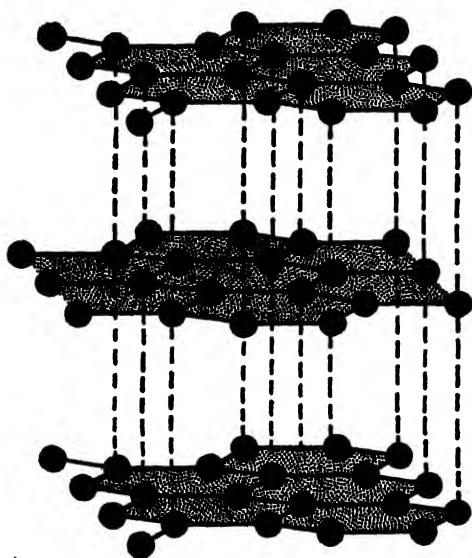
Graphite. Graphite is a shiny, gray-black form of carbon which feels slippery when it is rubbed between the fingers. Because of its platelike crystals and ready cleavage it is used to some extent as a lubricant. It cleaves easily due to its crystal structure, in which carbon atoms are close to each other in two dimensions and relatively far apart in the third, i.e., graphite consists of planes of carbon atoms rather widely separated, as shown in Figure 10.2. These planes of carbon atoms are held together weakly, hence can readily be made to slide past one another, and become separated with but little effort.

Graphite is found in nature, and mined (most of our natural graphite comes from Mexico), but there is also demand for the manufactured product. It is made by heating coke and coal in an electric resistance furnace. When an electric current is passed through the mixture the resistance is such that an extremely high temperature is reached, in the neighborhood of 4000°C . Carbon sublimates at this temperature and recondenses in the form of graphite.

Graphite finds many uses. Since it resists chemicals and has a high thermal stability crucibles and special pipe are made from it. It is employed as a lubricant, both by itself and in various mixtures. It is used in electrodes because, unlike most nonmetals, it is a fair conductor of electricity. It is one of the ingredients present in pencil leads, particularly in the softer types, and the



(a)



(b)

word "graphite" comes from the Greek "to write." Another, modern use for graphite is in the uranium pile (page 300).

Diamond. A second, rare form of crystalline carbon is the diamond. Its crystalline structure is shown in Figure 10.2 and is seen to be very different from that of graphite. It is interesting to note the extreme differences in physical properties shown by the two crystalline forms of this element. Graphite is opaque, a fairly good conductor of electricity, and one of the softest substances known. The diamond is transparent when pure, a very poor conductor of electricity, and the hardest natural substance known. This hardness is due to the strong bonds between carbon atoms. All of the carbon atoms' outer electrons are used in these covalent bonds,

as shown by the lack of electrical conductance.

Diamonds are found in nature most prolifically in South Africa and Brazil, and also in smaller numbers in many other places. Occasional diamonds have been found in this country in Arkansas, California, North Carolina, Virginia, Ohio, Indiana, and Wisconsin. In the last three states named they are thought



FIGURE 10.3. Graphite Manufacture. Electric furnaces used to convert amorphous carbon to graphite. Courtesy National Carbon Division, Union Carbide and Carbon Corporation.

to have been carried in with glacial drift from Canada. Diamonds are apparently formed as the result of high temperatures and high pressures, because small diamonds have been made this way by man, although these are not of sufficient size to compete with the natural stones. In the richest diamond regions, in South Africa, the stones are found in a “blue ground” matrix which fills the necks of extinct volcanoes. They apparently crystallized, at high temperature and pressure, from an igneous rock which later weathered to this matrix. This is removed, the earth crushed, and the diamonds separated by use of water and grease plates, which catch and retain the diamonds.

The unit of weight used in the diamond industry is the carat (0.2 gram), not to be confused with the carat employed to express the purity of gold (pure gold, 24-carat). The largest diamond ever found, the Cullinan, had a mass of 3024 carats, or about 1.3 pounds. It no longer exists as a single stone, having been cut into a number of smaller diamonds, some of which are nevertheless huge as diamonds go (Cullinan I, 516 carats, Culli-

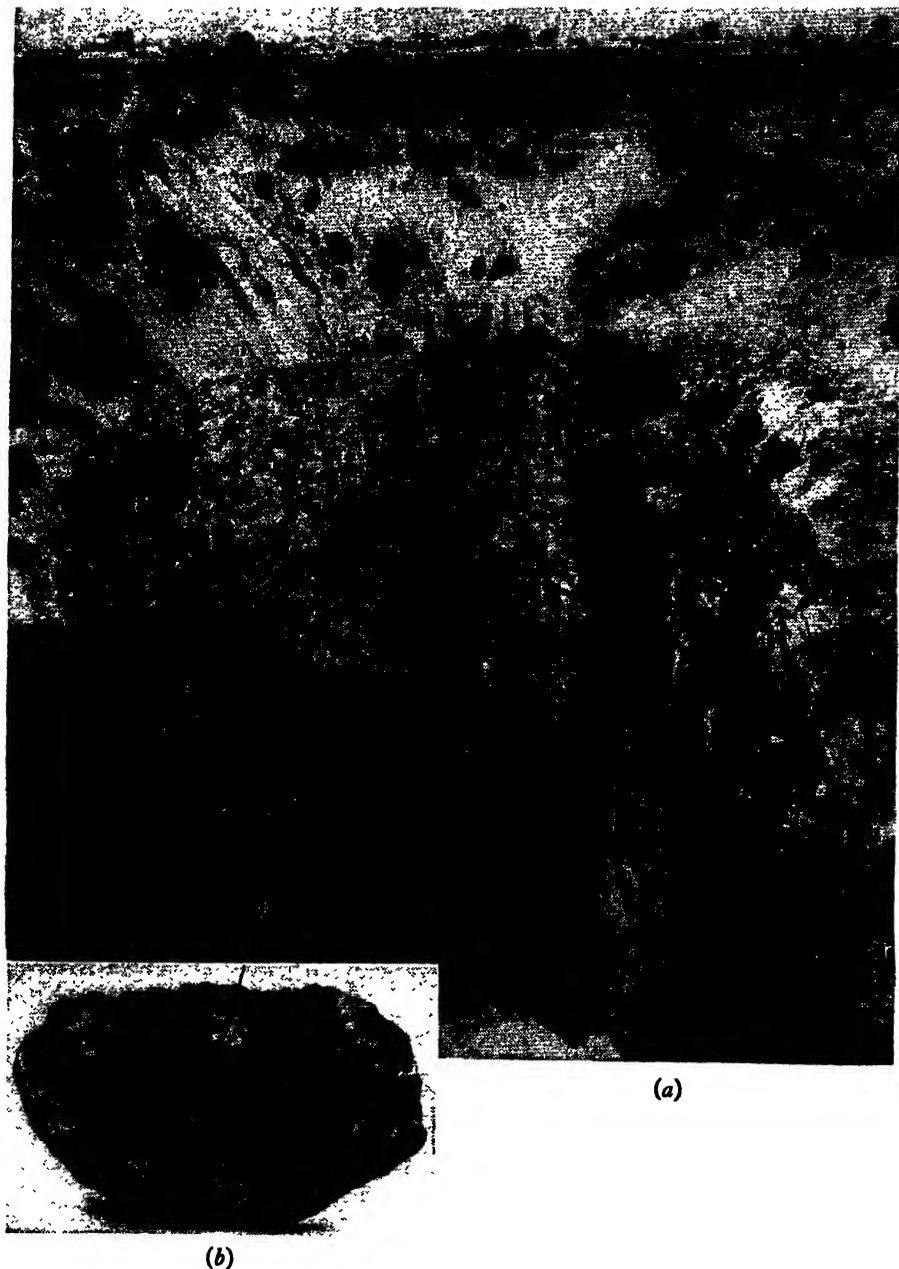
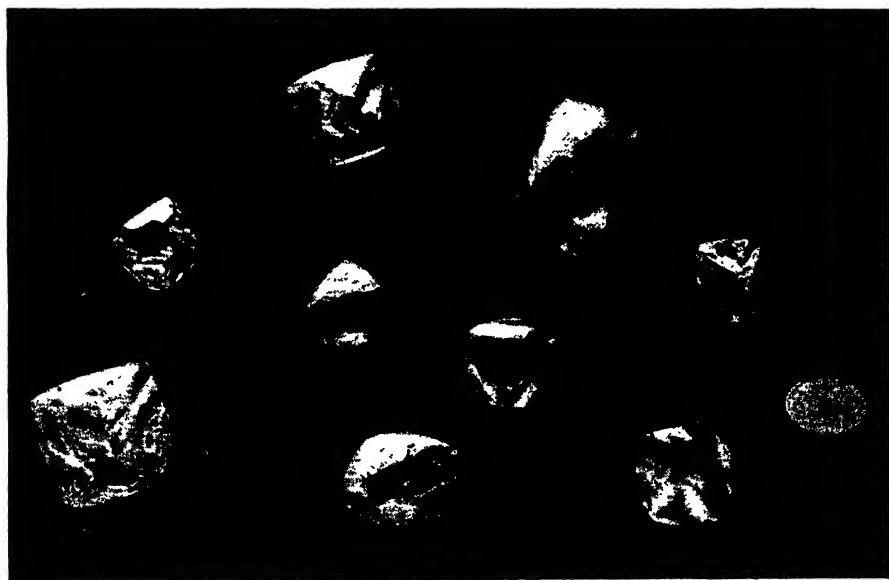


FIGURE 10.4. Diamond Mining. (a) The Kimberley "Pipe" Mine, one of the largest man-made holes in the world. Twenty-five million tons of rock were excavated before shaft mining was started. (b) Blue ground from this mine, containing diamond. Courtesy Gemological Institute of America.



(a)



(b)

FIGURE 10.5. Diamonds. (a) Ten days' production from a diamond mine. This represents nearly a million dollars worth of diamonds. (b) Rough gem diamonds. Courtesy Gemological Institute of America.

nan II, 309 carats, both in the crown jewels of England). Some diamonds are colored, and if this is pleasing or striking it en-

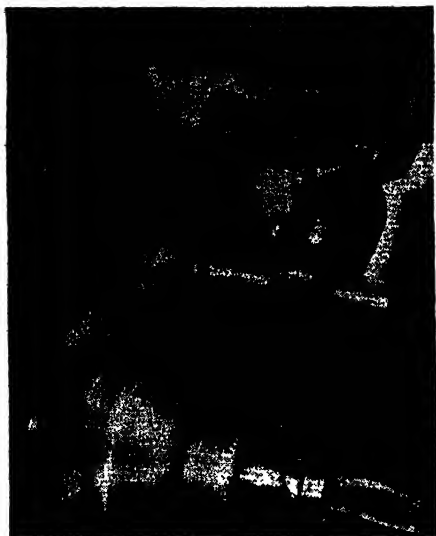


FIGURE 10.6. Diamond Sawing. Most diamonds are sawed rather than cleaved today. The phosphor-bronze blade, 0.0035 inch thick, is impregnated with diamond dust. Courtesy Gemological Institute of America.

hances the value of the stone. Thus, the Hope diamond (blue), the Tiffany (orange yellow), and the Florentine (pale yellow) are all of greater value because of their color. Some diamonds are black, and have no gem value, but are nevertheless in demand because of their hardness. They are used in the saws and drills employed for cutting stone, and in powdered form for polishing hard materials, including other diamonds.

Some of the world's famous diamonds are very old, and have histories replete with theft and bloodshed. The Kohinoor (108 carats) for example, at present one of the crown jewels of England, has been traced back to about the year 1000, when it was probably in the family of the Rajah of Malwa, and it is thought that it may have belonged to the legendary Indian Karna, who lived some ten or twelve centuries before that. From the Rajah of Malwa it is believed to have passed to Sultan Ala-el-din, the Mogul emperor Baber, the Persian Nadir Shah, the Afghan Ahmed, the Indian Runjit Singh, and finally to the East Indian Company, who presented it to Queen Victoria.

Even the clearest and most transparent diamonds are not outstanding in appearance in the rough state. To bring out their best light-reflecting qualities diamonds must be cut and polished by experts whose work requires great skill. The manner of cutting is determined by the position of the natural cleavage planes of

the stones. The center of the diamond cutting and polishing industry was in Amsterdam and Antwerp for many years, but a considerable amount of the work is now done in this country.

The properties of diamond and graphite are contrasted in Table 10.1.

TABLE 10.1 Properties of Diamond and Graphite

	<i>Diamond</i>	<i>Graphite</i>
COMPOSITION	Carbon	Carbon *
COLOR	Colorless; refractive index high (2.4195).	Black
HARDNESS	Hardest natural substance known. 10 on hardness scale.	One of softest substances known. 1 to 2 on hardness scale.
DENSITY	3.5 g. per cc.	2.2 g. per cc.
ELECTRICAL CONDUCTANCE	Very poor*	Fair*
CHEMICAL ACTIVITY	Inactive at low temps. Combines with oxygen at high temperatures.	Inactive at low temps. Combines with oxygen at high temperatures.

* A single graphite crystal has about 3 per cent the electrical conductance of copper, while diamond has only 10⁻²⁰ the conductivity of copper.

Other Forms of Carbon. In addition to the crystalline graphite and diamond, other, less pure, forms of carbon are known which are either amorphous or have such tiny crystals that their presence can only be shown by use of X-ray. The reader is familiar with a number of these forms. Coal is the commonest, and will be considered later. Products which are chiefly carbon are made by burning natural gas or other carbon compounds with a limited supply of air. These include carbon black, lampblack, and gas black. They are made by allowing a smoky flame to cool, as by coming in contact with a cold, revolving drum. The carbon deposits on the drum and is continuously scraped off. Finely divided carbon prepared in this way is used chiefly in the making of automobile tires, and also

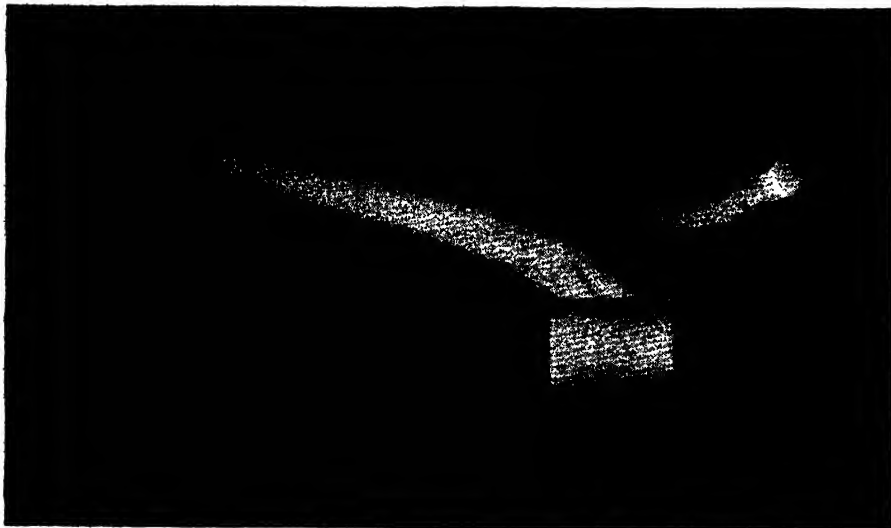


FIGURE 10.7. Uses of Carbon. The arc light, employing two carbon electrodes. Courtesy National Carbon Division, Union Carbide and Carbon Corporation.

in inks, paints, carbon paper, phonograph records, shoe polish, and in general where a permanent black color is desired.

Charcoal is another impure form of carbon made by heating wood in the absence of air. It finds use as a fuel and as an adsorbent, the latter because of its porosity and large surface. It is employed for adsorbing undesirable gases (as in gas masks) and for adsorbing impurities from liquids (as in purifying sugar solutions). Another widely used adsorbent is bone black, or animal charcoal. It is made by heating bones and other animal parts in the absence of air. This product contains a considerable amount of calcium phosphate, hence is very impure carbon. Another form of carbon, coke, will be mentioned later (page 310).

Inorganic Compounds of Carbon in the Earth's Crust.

Carbon compounds in the earth's crust are chiefly carbonates, i.e., metal salts containing the CO_3 radical, such as calcite (CaCO_3), dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), magnesite (MgCO_3), siderite (FeCO_3), azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), and many others. The commonest rock containing carbonates is *limestone*, chiefly calcium carbonate (minerals like calcite are usually pure



FIGURE 10.8. Uses of Carbon. Carbon electrodes are used in this electric furnace for producing steel. Courtesy National Carbon Division, Union Carbide and Carbon Corporation.

substances whereas a rock may be a mixture of minerals, such as granite or limestone).

Limestone was laid down in the geological past as the result of the accumulation of tremendous numbers of shells from organisms in sea water. The thick shell layers were in some cases elevated, following upheavals of the ocean floor, and became part of the land mass above sea level. A piece of limestone, examined with a microscope, can be seen to consist of an aggregate of shells or shell fragments, if it has not been too badly altered by heat and pressure.

The calcium carbonate which chiefly makes up limestone undergoes several important chemical changes. It is decomposed by heat, forming calcium oxide or *quicklime* (CaO) and carbon dioxide. The process is carried out in a limekiln.



It is acted upon by strong acids, also yielding carbon dioxide.



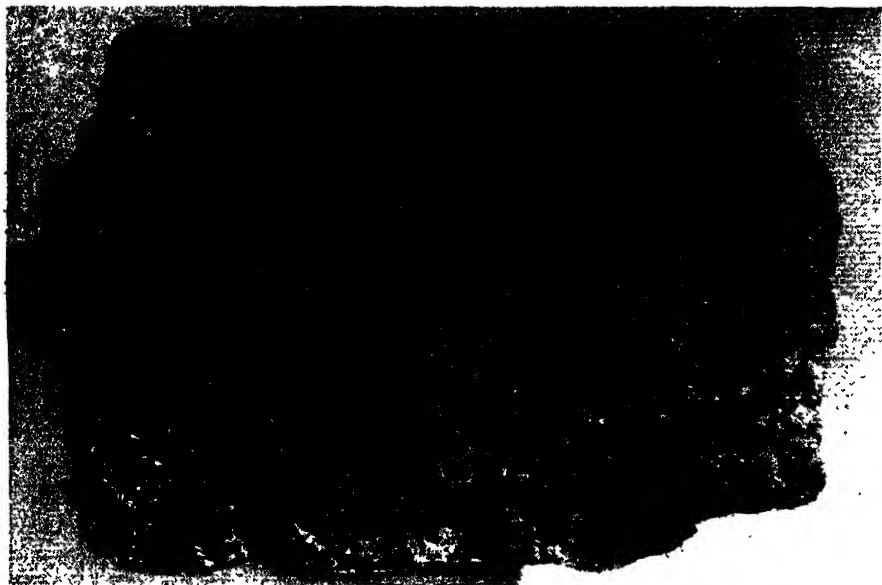
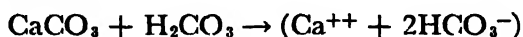
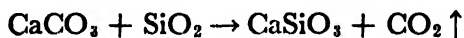


FIGURE 10.9. Limestone, Showing Shell Content. Courtesy Ward's Natural Science Establishment, Inc.

It is converted by *carbonic acid* to the soluble calcium bicarbonate, and in this way we account for the formation of limestone caves by action of natural waters containing carbonic acid upon limestone.



Calcium carbonate reacts with silicon dioxide at high temperatures to form calcium silicate, as described in the discussion of glass making. The same reaction probably occurs in nature, when limestone and silica are in contact in regions where volcanic activity causes a sufficient elevation of temperature.



PHOSPHORUS

Occurrence and Preparation. Because of its chemical activity the element phosphorus does not occur free in nature. It is found chiefly as calcium phosphate (phosphorite, phosphate rock), and as a combination of this salt with calcium fluoride or

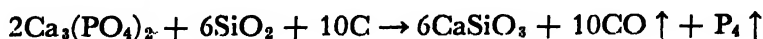


FIGURE 10.10. Concentration Plant for Phosphate Rock. Mixture of water and impure phosphate rock is piped into this plant. The phosphate rock is mostly separated (therein) by flotation, but some finely divided material is not recovered until suspension has stood in the two settling basins shown. Washed, concentrated phosphate rock is carried by railroad cars to drying and grinding mills. Courtesy American Cyanamid Company.

calcium chloride (apatite). These minerals are usually associated with fossils, and it appears that bones of prehistoric animals may have been the source of much of our present phosphate deposits. In this country phosphate rock is found chiefly in the five states of Tennessee, Florida, Idaho, Wyoming, and Montana.

Phosphorus was first prepared (in 1669) by Brand, a German alchemist, from urine. The process was complex, and long kept a secret, because the element was regarded as being of special significance, due to its property of glowing in the dark.

Phosphorus is now made by heating calcium phosphate with silica and carbon.



Modifications of Phosphorus. The phosphorus vapor formed by reducing calcium phosphate consists of tetratomic molecules

(P_4) in which phosphorus atoms occupy each corner of a tetrahedron.¹ When the vapor cools it condenses to the white form of solid phosphorus (also called yellow phosphorus because its original light color darkens a little with age). This ignites so

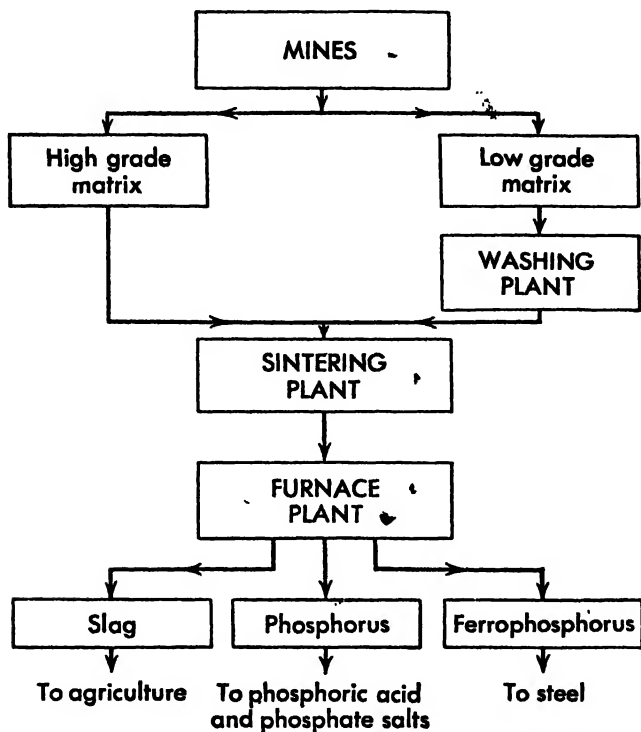


FIGURE 10.11. Manufacture of Phosphorus. Flow of materials during conversion of phosphate rock to phosphorus and other substances. Courtesy Monsanto Chemical Company.

readily in the air that it is usually kept under water. White phosphorus changes to another variety—red phosphorus—when heated moderately. The latter is a much less active form of the element. Two other forms of phosphorus have been made, violet and black. Violet phosphorus appears to differ signifi-

¹ According to the rule of eight, each phosphorus atom must share pairs of electrons with the other three atoms in the tetrahedron and retain two unshared. This arrangement requires 12 shared electrons and eight unshared for a total of 20 electrons. Since each phosphorus atom has five outer electrons, there are 20 electrons available in a four atom molecule.

cantly from the red modification only in color. Black phosphorus seems to be another distinct type which can be prepared only under high pressure. The reactivity of the different forms decreases as the color darkens. White phosphorus is exceedingly poisonous, but the other solid forms appear to be relatively harmless.

Properties of Phosphorus. Physical properties of phosphorus are shown in Table 10.2.

TABLE 10.2 Physical Properties of Phosphorus

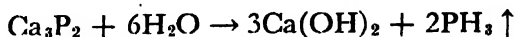
	<i>White phosphorus</i>	<i>Red phosphorus</i>	<i>Violet phosphorus</i>	<i>Black phosphorus</i>
COLOR	Colorless when pure	Red	Violet	Black
DENSITY	1.8	2.3	2.3	2.7
KINDLING TEMP.	About 30°C.	About 260°C.	—	—
MELTING POINT	44°C.	About 600°C.	620°C.	—
ODOR	Garlic-like	None	None	None
SOLUBILITY IN CARBON DISULFIDE	Soluble	Insoluble	Insoluble	Insoluble

When phosphorus burns it is converted to either P_4O_6 or P_4O_{10} ,² depending upon the amount of oxygen available. White phosphorus in contact with air and water undergoes oxidation slowly even at room temperature, in an unusual change accompanied by the emission of cold light (phosphorescence), and it is to this phenomenon that phosphorus owes its name.

The element reacts with metals to form phosphides. With calcium:



Calcium phosphide in turn reacts with water to form the very poisonous gas *phosphine*.



² These oxides can be considered as being formed from the P_4 tetrahedron. In P_4O_6 one oxygen atom is between each of the six possible pairs of phosphorus atoms in the tetrahedron. In P_4O_{10} an additional oxygen atom is held, outside the tetrahedron, by each phosphorus atom.

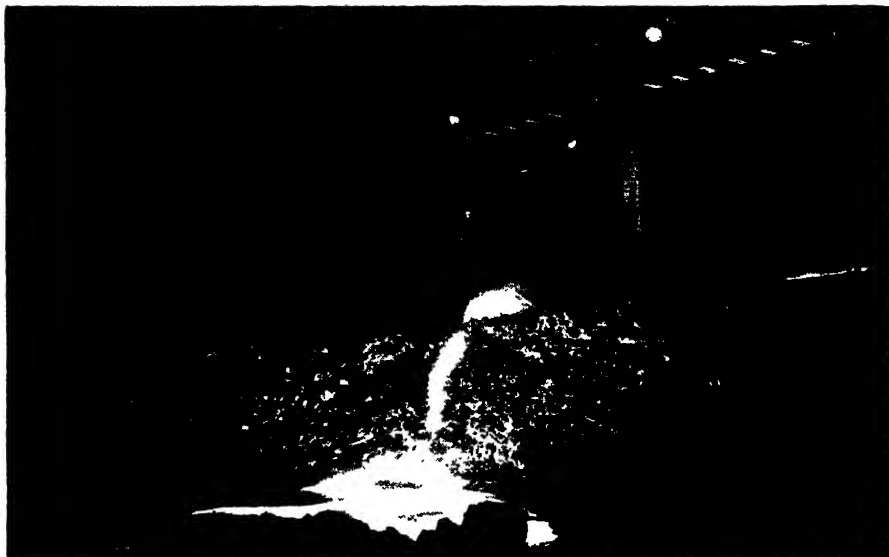


FIGURE 10.12. Manufacture of Phosphorus. Slag is being run off. Courtesy Monsanto Chemical Company.

Phosphorus combines with excess chlorine to form solid phosphorus pentachloride.



Uses of Phosphorus and Its Compounds. The element itself is used in making compounds, such as the sulfide and chloride. White phosphorus is employed in pyrotechnics, incendiary bombs, and as a source of chemical smoke. Red phosphorus is present in the mixtures which make up the striking surfaces for safety matches.

The compounds of phosphorus are used in fertilizers (calcium acid phosphates), as water softeners (trisodium phosphate), in baking powders of the phosphate type, and in matches. Orthophosphoric acid has already been mentioned (page 157).

Matches. The strike anywhere match has on its tip a small amount of phosphorus trisulfide (P_4S_3). This substance has such a low kindling temperature that it is ignited by friction, and in turn it lights the rest of the match head, which consists of combustible material such as rosin or paraffin, oxidizing agents such

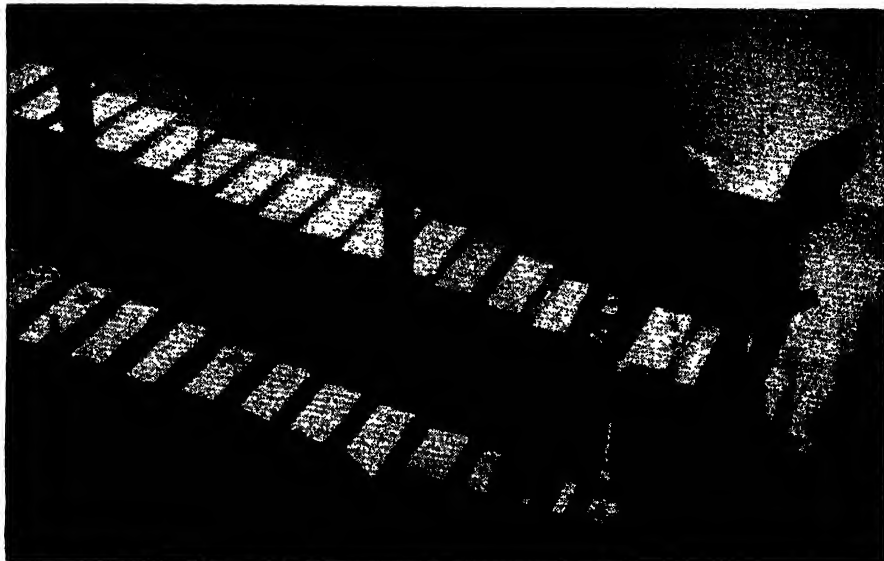


FIGURE 10.13. Ferrophosphorus. Made from phosphate rock, this is used in some steels. Courtesy Monsanto Chemical Co.

as potassium chlorate, fillers such as clay, a glue binder, and usually a coloring material. The match stick is often dipped in a salt solution during manufacture to slow up its burning rate and prevent after-glow.

Matches used to contain yellow phosphorus in the head, but the substance created a fire hazard, and in addition workmen handling this chemical were often subject to a deterioration of the lower jaw, an affliction known as “phossy jaw,” which probably resulted from getting phosphorus in the mouth from the hands while eating, and from the inhalation of phosphorus vapor. This condition became so prevalent among people handling yellow phosphorus that in 1913 the government made its use unprofitable by levying a heavy tax upon this type of match.

The safety match usually contains antimony sulfide and an oxidizing agent in its head. The striking surface placed on the side of the box consists of a mixture of red phosphorus, abrasive, and binder. When the safety match is struck on this prepared surface a small amount of the phosphorus ignites and lights the match.



FIGURE 10.14. Mining Sulfur. Steam, from the boilers (1) heats water in jet type mine water heaters (2) to about 330° F. The hot water is pumped (3) down the outer of three concentric pipes into the sulfur formation (4) through openings in the pipe. The melted sulfur, being heavier than water, collects at the bottom (5) of the well. Compressed air (6) forces the liquid sulfur to the surface where it is collected in sumps (7). Pumps (8) lift the sulfur into the vats (9), where it solidifies and is later broken down for shipping. Courtesy Texas Gulf Sulphur Company.

SULFUR

Occurrence and Mining. Sulfur, or brimstone, as it is sometimes called, has probably been known to man from earliest times, since it occurs free in the earth's crust. (Sicily, Louisiana, and Texas have important deposits.) It is also commonly present in combined form as sulfides and sulfates of metals, as for example gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), pyrite (FeS_2), galena (PbS), and sphalerite (ZnS).

Sulfur was at one time obtained from surface deposits; chiefly in Sicily. The impure sulfur was made into piles and set on fire, and the heat caused the sulfur which did not burn to flow out in purer form. At present most of the world's sulfur is obtained from Louisiana and Texas by use of the Frasch process, in which sulfur is brought up from underground beds by taking advantage of its low melting point (112.8°C.) and density (2.07 grams per cc.). As shown in the drawing (Figure 10.14) water heated under



FIGURE 10.15. Sulfur Mining. Molten sulfur being pumped on top of a partially filled vat. Completed vat which has been blasted for loading into cars shown at left. Courtesy Texas Gulf Sulphur Company.

pressure to 170°C . is forced down the outer of three concentric pipes. This melts the sulfur. Air, forced down the innermost pipe, forms with the molten sulfur a froth which is lighter than water. A mixture of melted sulfur, water, and air is thereupon forced up the middle pipe, and in this way the sulfur is brought to the surface. There it is stored in huge piles until ready for shipment. Sulfur is at present (1952) in short supply, because of military demands both at home and abroad. The situation should be helped in the near future, however, by the recent discovery of a large, new sulfur deposit in Louisiana, on the lower Mississippi River delta. This is expected to yield half a million tons of sulfur annually when mining reaches full production in 1953.

Properties. Solid sulfur at room temperature exists as rhomb-shaped crystals (Figure 10.16). Hence it is known as *rhombic* sulfur. This form melts at 112.8°C . and has a density of 2.07

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grams per cc. If held at 95.5°C. or above for a time, or if molten sulfur is cooled, a second solid form, *monoclinic* sulfur, is made. This exists in crystals like those shown in Figure 10.16. Monoclinic sulfur melts at 119°C. Molten sulfur above this temperature

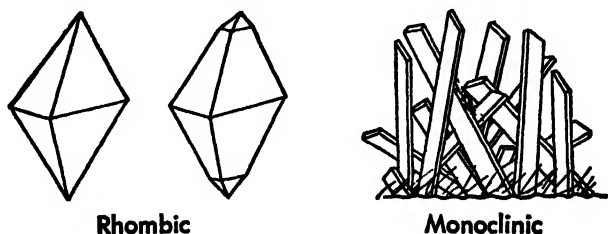
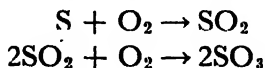


FIGURE 10.16. Crystalline Forms of Sulfur. Redrawn from Hopkins and Bailar, *Essentials of General Chemistry*, D. C. Heath and Company (1946).

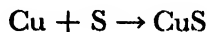
also exists in more than one form, and as a result the liquid behaves in an unusual manner as it is heated. It becomes more viscous with heat, up to about 200°C. Above this temperature it thins out again and boils at 444.6°C. Sulfur vapor exists as various polyatomic molecules. It is thought to become S_2 at high temperatures.

Sulfur burns in the air with a blue flame to form the dioxide which can then be further oxidized to the trioxide.

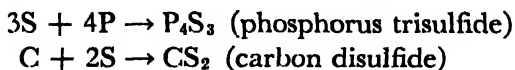


These reactions were mentioned under the contact process for making sulfuric acid (page 152).

Sulfur, like oxygen, combines in general with metals, to form sulfides.

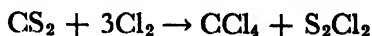


Nonmetals also react with sulfur; examples are the compounds formed with phosphorus and carbon.

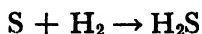


Phosphorus trisulfide is a yellow solid employed in the tips of strike anywhere matches. Carbon disulfide is a volatile liquid,

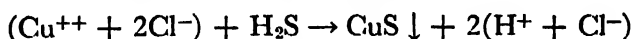
colorless, and with an unpleasant odor. It is used chiefly in the manufacture of the cleaning fluid and fire extinguisher *carbon tetrachloride* (CCl_4), which forms when it is treated with chlorine.



Sulfur reacts with hydrogen to form the gas hydrogen sulfide.



At high temperatures the reaction reverses. Hydrogen sulfide, a colorless gas with a disagreeable odor, has already been mentioned (page 92). It is widely prepared for use in qualitative analysis, but usually by action of hydrochloric acid upon ferrous sulfide, or by heating a mixture known as "Aitch-tu-ess." The metallic sulfides which can be made from it differ in their solubilities, hence can be separated from one another. For example, a mixture of cupric chloride and ferrous chloride can be separated by passing hydrogen sulfide through an acidified aqueous solution of the two salts. The copper sulfide precipitates and the ferrous chloride remains in solution.



Uses of Sulfur. Large quantities of sulfur are used in the preparation of sulfuric acid (page 152), the vulcanization of rubber (page 468), and mixed with lime as a fungicide, e.g., "lime-sulfur" sprays. Sulfur is also employed extensively in the preparation of other compounds containing the element. These include phosphorus trisulfide, carbon disulfide, sodium thio-sulfate, sulfur dioxide, and many organic sulfur compounds. It is used in both the free and combined state in a class of lubricants able to stand high pressures and high rubbing speeds, called extreme pressure lubricants.

Self Study Questions

1. What two crystalline forms of carbon occur in nature? How do they differ in physical properties? How do we account for the great difference in hardness between the two forms?

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2. How is graphite prepared commercially? What are the uses of this form of carbon?

3. The density of diamond is 3.5 g./ml. Calculate (a) the volume occupied by a gram atomic weight of carbon in diamond form, (b) the volume occupied by one carbon atom in diamond (Avogadro's Number needed).

Answers: (a) 3.4 ml., (b) 5.6×10^{-24} ml., or 5.6 cubic angstroms.

4. Give examples of minerals containing carbon in combined form. How were our present limestone deposits formed?

5. Write equations showing the effect of heat, strong acids, carbonic acid, and silica upon calcium carbonate.

6. A liter of gas is made up of equal numbers of oxygen and nitrogen molecules. This is passed over excess hot carbon, causing all of the oxygen to be converted to carbon monoxide. The resulting mixture of gases is then brought to the original temperature and pressure. What is the final volume?

Answer: 1.5 liters.

7. How does phosphorus occur in nature? What is thought to be the source of these deposits?

8. Write an equation showing the reaction which takes place when phosphorus is obtained from calcium phosphate.

9. What two types of phosphorus are of importance? How do they differ in properties?

10. Explain how the rule of eight is satisfied in the P_4 molecule.

11. Write equations showing how phosphorus reacts with metals, nonmetals.

12. Name four important compounds of phosphorus and give one or more uses for each.

13. Discuss the composition and changes upon ignition of safety and strike anywhere matches. What is the objection to yellow phosphorus in matches?

14. Discuss the occurrence of free and combined sulfur. How is sulfur obtained in the Frasch process?

15. What two solid forms of sulfur are known? Which is the stable form at room temperature?

16. Show by equations the reactions of sulfur with metals, nonmetals.

17. What are some important uses of sulfur? Name three or more materials in the home which contain sulfur.

18. What weight of sulfur would have to be oxidized to sulfur trioxide so that the latter substance would react with water to form one liter of sulfuric acid solution of density 1.32 g./ml. containing .42 per cent H_2SO_4 by weight? *Answer: 181 grams.*

XI

Some Familiar Metals

Occurrence. A few of the less active¹ metals, such as gold and silver, occur free in the earth's crust, but the great majority are present in combined form as silicates, sulfides, carbonates, oxides, and other compounds. Rocks containing metals or metallic compounds which can be treated so as to profitably yield the metals are known as *ores*. In general all of the common metallic compounds except the silicates fall into this category. Extraction of metals from the silicates is usually too costly to be profitable, which is unfortunate, since the silicates are by far the commonest compounds of some metals occurring in nature, as for example aluminum.

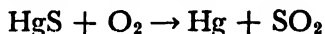
Considering the earth as a whole, it may well be higher in metal content than is apparent from examination of its surface. It is thought that its core, starting at a depth of about 1800 miles, may be composed of metallic iron and nickel. This would make the earth agree approximately in composition with the average shown by many meteorites, since a number of these are metallic while others have a composition similar to that of our surface rocks. This metallic core would also account for the high density of the earth (5.5), much higher than that of the surface rocks (2.7), and would help to explain why the data obtained from study of earthquake shock records show an abrupt change

¹ An active metal is one whose atoms readily lose electrons and become ions, or conversely, one whose ores (electrovalent substances containing ions of the metal) are difficult to change to the free metal. The most inactive metals tend to keep all their electrons and remain in nature as free metals.

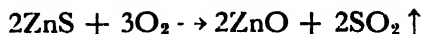
at a depth of about 1800 miles from substances permeable to quake vibrations to something which weakens them considerably.

GENERAL METALLURGICAL PROCESSES

Reduction of Ores. The treatment which an ore is given to obtain the free metal depends upon a number of factors, e.g., the type of ore, the activity of the metal, available resources for metallurgy, and the amount of metallurgical research which has been done. Except for metals in the free state, the general process is one of *reduction*, or removal of elements or radicals associated with the metal in the ore. In the change which takes place the metal atoms gain electrons and become the free metal. For compounds of inactive metals, this is sometimes brought about by merely heating the compound in the air. Thus, in the case of mercury, the sulfide *cinnabar* is often converted to metallic mercury in this way right at the mine.



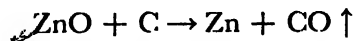
Reduction with Carbon. A common procedure in the case of many ores is to convert them to oxides and then reduce with some form of carbon. Sulfide ores, for example, are heated in the presence of air (roasted).



Carbonates, similarly heated, lose carbon dioxide.

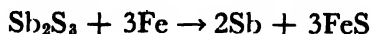


The oxides can then be reduced with carbon.



Reduction with Electricity. The use of electricity is growing in metallurgy. It is employed exclusively in the electrolytic preparation of the most active metals, such as sodium (page 136) and aluminum (page 230). It is being used to an increasing extent for deposition of less active metals from water solutions of their salts. Thus, zinc oxide is now frequently dissolved in dilute sulfuric acid, and the solution electrolyzed, yielding zinc and regenerating sulfuric acid.

Reduction with Another Metal. A final metallurgical process which should be mentioned is the displacing of the desired metal by a cheaper metal. Antimony, for example, is made by heating its sulfide *stibnite* with iron.



GENERAL PROPERTIES OF METALS

Physical Properties. Metals are opaque substances except when in very thin films, solid at ordinary temperature (except mercury) and capable of acquiring a characteristic luster. In general they conduct heat and electricity well. They can be hammered into thin sheets (malleability) and drawn into wires (ductility). Most metals have a greater density than average substances, e.g., a sample of iron will weigh about three times as much as an equal volume of sand. However, individual metals vary greatly in their densities, from lithium, half as dense as water, to osmium, 22.5 times as dense. There are many more metals than nonmetals, since about three quarters of the elements are in the former category. Some information about the metals to be discussed is given in Table 11.1.

TABLE 11.1 Properties of the Metals

Metal	Density grams per cc.	Appearance	Melting point °C.	Boiling point °C.	Electrical*		Approximate price per pound
					A	B	
ALUMINUM	2.70	silver	660	1800	8.3	34.9	\$ 0.17
ZINC	7.14	blue-white	419	907	3.7	5.9	0.13
CHROMIUM	7.1	blue-white	1615	2200	8.3	13.3	0.25
IRON	7.86	silver	1535	3000	2.2	3.2	0.02
TIN	7.30	silver	232	2260	1.9	3.0	1.40
LEAD	11.34	silver	328	1620	1.0	1.0	0.16
COPPER	8.92	reddish	1083	2300	12.8	16.6	0.19
MERCURY	13.55	silver	-38.9	356	0.2	0.2	1.05
SILVER	10.5	silver	960	1950	13.5	9.1	10.51
GOLD	19.3	yellow	1063	2600	9.1	5.4	511.00

* Electrical conductance (A) is for wires of the same diameter, calling lead 1.0. On this basis, for example, silver is the best conductor, 13.5 times better than lead. Electrical conductance (B) is for wires, equal lengths of which have the same weight. On this basis aluminum is the best conductor of the metals listed, 34.9 times better than lead.

Activity Series. Metals have a characteristic atomic structure in that the outer electron shell, with a few exceptions, contains less than four electrons. They also behave characteristically by readily losing these electrons and forming positively charged ions, such as Na^+ , Ca^{++} , or Al^{+++} . However, different metals vary considerably in the ease with which they lose their outer electrons. Metals which lose them most easily, such as sodium, are called active, since they react with (i.e., lose electrons to) many substances, giving off much heat and even light in the process. Other metals, like lead, part with their outer electrons less readily, and still others, such as gold and platinum, lose them still more reluctantly. It is possible to arrange the metals in a series, called the *activity series*, in which the members are listed in the order of decreasing tendency to form ions in water solution, so that the lower the position in the series the more firmly the metals hold their outer electrons. Such a series is given in Table 11.2.

Displacement. The activity series is seen to contain hydrogen. While this element is not a metal in its other properties, its atoms lose their electrons readily, behaving like a metal in this respect. Another point of interest is that the metals in this series will displace from water solution other metals or hydrogen below them, i.e., they give their outermost electrons to metal ions below them, causing the latter to change to the free metal and the more active metal to become an ion. Thus, a piece of copper immersed in a mercuric nitrate solution will cause mercury to deposit on the copper giving it a silvery appearance, and copper ions will be formed in proportional amount in the solution, causing the latter to turn blue.

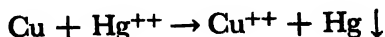
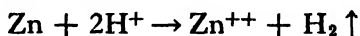


TABLE 11.2
Activity Series

LITHIUM
POTASSIUM
SODIUM
BARIUM
STRONTIUM
CALCIUM
MAGNESIUM
ALUMINUM
MANGANESE
ZINC
CHROMIUM
CADMIUM
IRON
COBALT
NICKEL
TIN
LEAD
HYDROGEN
COPPER
ANTIMONY
MERCURY
SILVER
PLATINUM
GOLD

The preparation of hydrogen by the action of acids upon active metals is another example of the same thing. Hydrogen ions are converted to free hydrogen and the metal is converted to its ions. Thus, when zinc is acted upon by hydrochloric acid the fundamental change can be written:



Reactions of this type are known as *displacements*.

In summary, then, an important property of metals is that their loosely held outer electrons are readily lost to nonmetals, as in the *combination* of sodium and chlorine, or of iron and oxygen, and also to other metals or hydrogen, as in the *displacements* just mentioned.

Electrical Conductance in Metals. These same loosely held electrons are also easily transferred from one metal atom to the next—like a line of men at a fire in the country passing along buckets of water from the well to the fire. This process takes place in a metal wire, when an electron pressure is exerted at one end and an electron shortage is created at the other, as when the wire is connected to a battery. The electrons passing through the wire then constitute the electric current, and in this way we account for the excellent electrical conductance of metals.

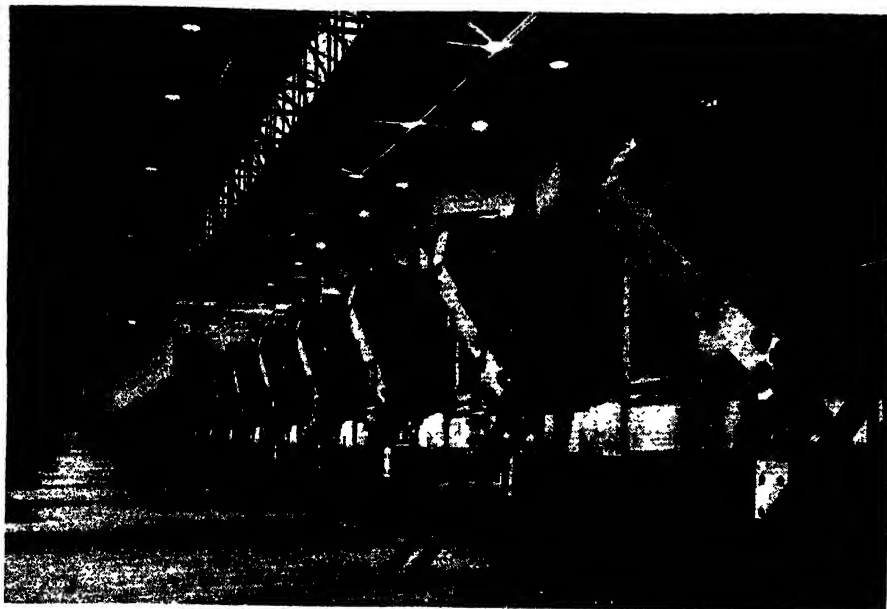
A L U M I N U M

Occurrence and Metallurgy. Aluminum is the third most abundant element in the earth's crust (page 28), and the most abundant metallic element. Such common minerals as clay and feldspar contain it in the form of the silicate. Metallic aluminum is more expensive to obtain from its silicate minerals, however, and in the important aluminum industry, *bauxite*, consisting of hydrated alumina ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) together with the oxides of iron, silicon, and titanium as impurities, is used for this purpose. The reduction process is an electrolytic one, discovered in 1886 by Charles M. Hall, who worked in the family woodshed at Oberlin, Ohio, shortly after graduation from Oberlin College.

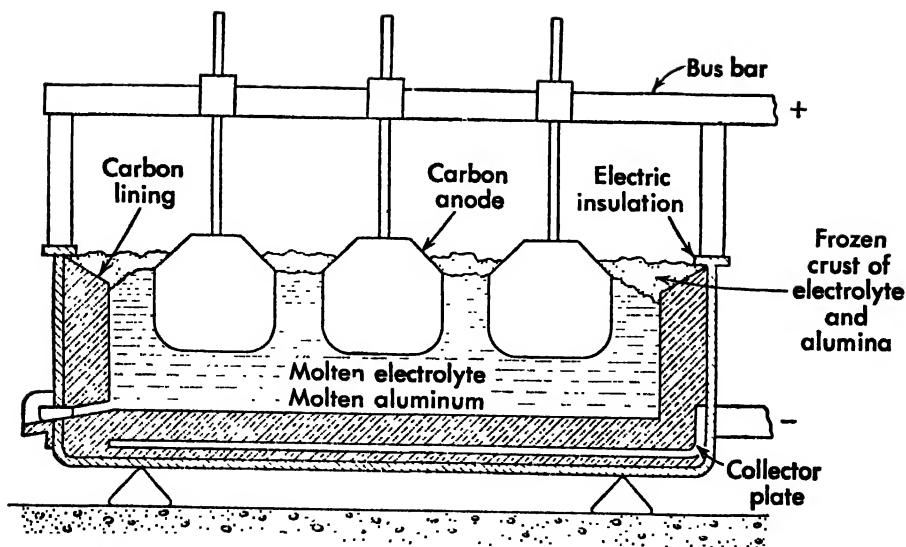
In this process pure aluminum oxide, prepared from bauxite ore, is dissolved in molten sodium aluminum fluoride (*cryolite*) at a temperature just below 1000°C . A high amperage electric current is then passed through the molten mass, causing metallic aluminum to deposit at the cathode, which is the carbon bottom of the container itself, and oxygen to be liberated at the anodes, which are rectangular carbon rods dipping into the bath. The temperature is maintained by the heat emitted during the electrolysis. Molten aluminum goes to the bottom of the container and is drawn off from time to time. The aluminum oxide is theoretically the only ingredient which is used up, and it is supplied intermittently as the electrolysis proceeds. In practice it is also necessary to add small amounts of cryolite from time to time, and to replace the carbon anodes, since these react with the oxygen liberated. The aluminum obtained is better than 99 per cent pure. It is prepared so economically today that the price has been as low as 15 cents per pound, as compared to earlier prices of \$160 per pound in 1828, \$27 per pound in 1858, and \$8 per pound in 1886.

Bauxite used in the electrolysis comes chiefly from Arkansas in this country and from Surinam in South America. The iron oxide and silica associated with this mineral must be removed before it is put in the electrolytic bath. Cryolite occurs mainly in Greenland, but a considerable amount of this is now manufactured rather than mined.

Properties of Aluminum. A number of physical properties of aluminum are given in the table on page 228. It is seen to be the least dense of the metals listed. It is ductile and workable between about -250°C . and $+500^{\circ}\text{C}$. A fresh surface of aluminum has a silvery white appearance. It quickly becomes covered with a tightly adhering and impervious coat of aluminum oxide, but a smooth surface still remains highly reflective, as in the case of aluminum mirrors. The fact that the oxide coating on aluminum is adherent and impervious and hence protective, is important. If it were porous like that on iron (rust)



(a)



(b)

FIGURE 11.1. Electrometallurgy of Aluminum. (a) Row of electrolytic cells. (b) Cross section of one cell in which a molten mixture of bauxite and cryolite is electrolyzed. Courtesy Aluminum Company of America.

aluminum would corrode rapidly, because of its high activity. The purity of aluminum may also affect its rate of corrosion.²

Aluminum mixes with most of the other important metals in the molten state. Some of these mixtures, upon cooling, have properties which make them more valuable for certain purposes than pure aluminum. Thus, aluminum containing small amounts of copper, manganese, and magnesium (duralumin) has a strength equal to that of structural steel. Other elements added in various combinations with aluminum are zinc, silicon, iron, and chromium. A mixture of metals prepared in the molten



FIGURE 11.2. Extruding Aluminum. A hydraulic ram forces an ingot through a die, causing the metal to take the shape of the opening in the die. Courtesy Aluminum Company of America.

state and allowed to cool is called an *alloy*. These are so important that the number of alloys in use vastly exceeds the number of pure metals. The composition of some familiar alloys is given in Appendix C.

Three shells of electrons surround the aluminum nucleus. Going out from the center these contain 2, 8, and 3 electrons. When the aluminum atom becomes an ion the three outer electrons are lost, hence the electrovalence of aluminum is three. This valence is exhibited in such compounds as aluminum chloride, aluminum sulfate, alum, and aluminum oxide.

Aluminum Compounds. Aluminum chloride in the anhydrous form (AlCl_3) finds important use as a catalyst in many organic syntheses. Aluminum sulfate, usually sold as the hydrate $\text{Al}_2(\text{SO}_4)_3 \cdot$

² See metal couples, page 241.

$18\text{H}_2\text{O}$, is now utilized in many of the mixtures and processes which formerly employed alum, such as in fire extinguishers (page 88), water purification (page 120), and baking powder. It is made by treating clay with sulfuric acid.

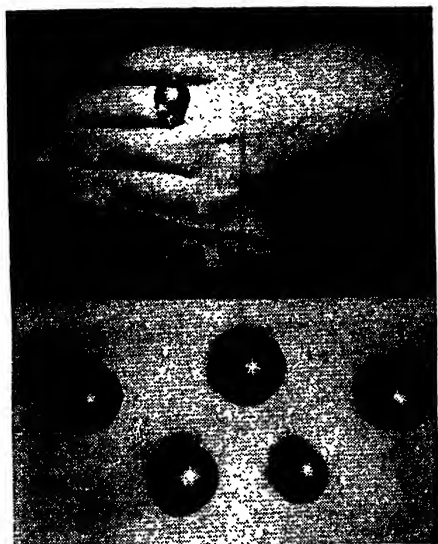


FIGURE 11.3. Forming an Aluminum Alloy Propeller Blade by Press Forging. Courtesy Aluminum Company of America.

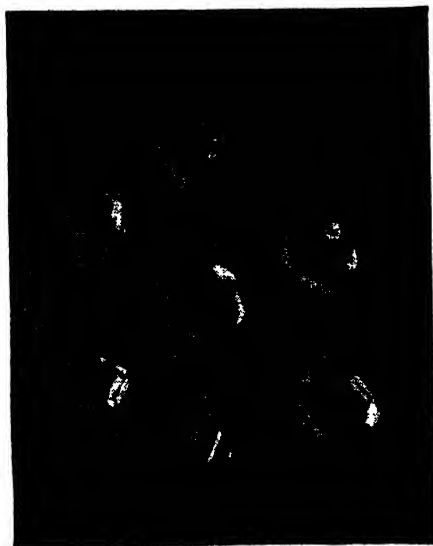
An *alum* is a general type of substance consisting of a hydrated double sulfate of a trivalent and a univalent metal. The term originally meant hydrated potassium aluminum sulfate, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, or as sometimes written, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. However, other univalent metals, such as sodium, cesium, rubidium, or silver, may be used instead of potassium, and other trivalent metals, such as iron, chromium, or manganese, may be

substituted for aluminum. The alums are a class of double salts which crystallize in the same system. Indeed, a crystal of one alum can be placed in a saturated solution of another, where it will continue to grow as the solution evaporates.

An interesting compound of aluminum is the oxide, Al_2O_3 . This occurs in nature as the mineral *corundum*, and in impure form as *emery*. Both are used as abrasives. Gem forms of aluminum oxide are also found in nature, notably the sapphire, ruby, and topaz. Certain types of amethyst are aluminum oxide, although ordinary amethyst is colored quartz, SiO_2 . These gems can now be made synthetically. Aluminum hydroxide is precipitated and heated to convert it to the oxide, traces of other oxides are added to give color, and the whole is melted and allowed to cool slowly. The crystals which form are chemically similar to the natural stones, but there are usually slight de-



(a)



(b)

FIGURE 11.4. Aluminum Compounds. (a) Synthetic sapphires, gem forms of aluminum oxide. (b) Ammonium alum crystals, $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.



FIGURE 11.5. Topaz Crystals. This is a gem form of aluminum fluosilicate. Courtesy Ward's Natural Science Establishment, Inc.

tectable differences. Sapphire in its purest form is simply crystalline aluminum oxide. Blue sapphire contains traces of the oxides of iron, titanium, cobalt, and chromium. Yellow sapphire (oriental topaz) contains small amounts of iron oxide. Ruby is aluminum oxide containing chromic oxide. The compositions of some gem minerals are given in Appendix F.

Uses of Aluminum. Aluminum is popular because of its relatively low price, low density, high tensile strength, and resistance to corrosion. It is widely used, not only for kitchen utensils, but in a variety of other ways, as for example in wrapping, in place of the much more expensive tinfoil; in flashlight bulbs, because it burns in oxygen with a brilliant incandescence; as a flake-like pigment to make a silver paint; in power lines, because of its excellent electrical conductance, much the best of the metals being discussed, on a weight basis. In alloy form it is also a key structural metal in places where lightness is important as well as strength, as in aircraft and trucks.

Z I N C

Occurrence and Metallurgy. Zinc is an ancient metal. No one knows who first prepared it, but articles made of zinc and zinc alloys have been found in the ruins of cities which flourished before the birth of Christ. In the early days of chemistry it was confused with lead and tin, since all three metals are silvery and were prepared by reduction of their ores with carbon. It has been known as an individual metal for only about 250 years.

The simplest zinc ores occurring in nature are the sulfide (ZnS , *sphalerite*), the oxide (ZnO , *zincite*), and the carbonate (ZnCO_3 , *smithsonite*). Various silicates and complex oxides with other metals are also known. A considerable amount of zinc is now produced by electrolysis of zinc sulfate solution, obtained by treating zinc oxide with sulfuric acid. In another method, known as the furnace process, zinc oxide is reduced with carbon.

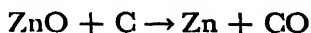




FIGURE 11.6. Electrolytic Zinc Production. Stripping zinc sheet off cathode. Courtesy Anaconda Copper Mining Company.

The temperature is made high enough so that the zinc distills. This is an unusual way in which to recover a metal. The boiling point of most metals is so high that vaporization is not feasible, but zinc boils at $907^{\circ}\text{C}.$, lower than any other common metal except mercury. Advantage is taken of this low boiling point to purify the metal by fractional distillation (page 316).

Properties of Zinc. A number of properties of zinc are given on page 228. The metal is seen to be about two and a half times as dense as aluminum, with relatively low melting and boiling points. Cast zinc is a brittle metal at ordinary temperatures, but becomes malleable and ductile when heated. In the rolled form zinc is ductile at room temperature. Zinc is a fairly active metal, well above hydrogen in the activity series. It does not corrode rapidly in the air because of a tightly adhering film of basic zinc carbonate which is thought to protect it in much the same manner as a film of aluminum oxide protects that metal. Zinc does not react rapidly with hot or cold water, but steam changes it to zinc oxide with the displacement of hydrogen.

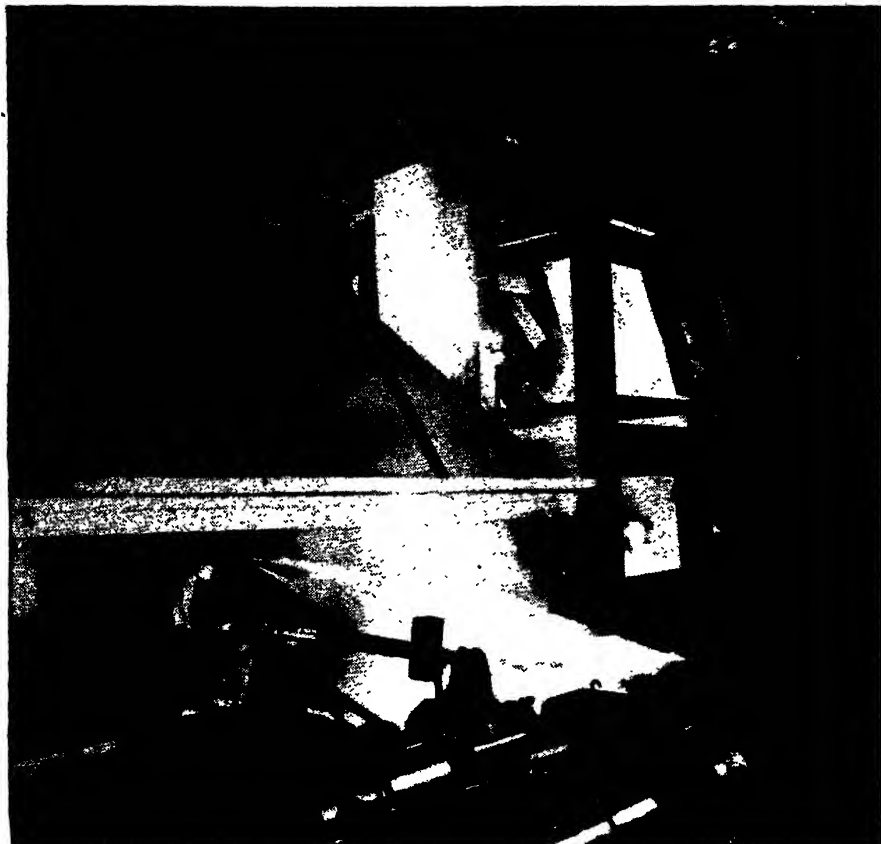
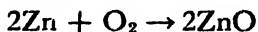
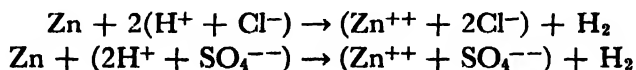


FIGURE 11.7. Modern Sheet Galvanizing. The sheet in the center of the picture has just come from the coating rolls, to be carried over the spangle control rolls and cooling ducts. Courtesy Wean Engineering Company.

If first heated sufficiently, zinc burns in air or oxygen with a brilliant blue-green flame.

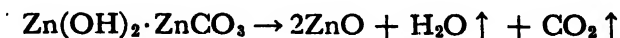


Zinc displaces hydrogen from hydrochloric and dilute sulfuric acids.



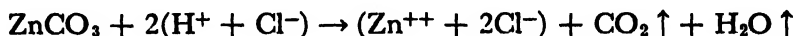
These reactions take place more rapidly if the zinc is in contact with some metal below it in the activity series (see *metal couples*, below).

Zinc Compounds. Four important zinc compounds are the oxide, chloride, sulfate, and sulfide. Zinc oxide is made by oxidation of the metal or the sulfide, or by heating the basic carbonate. The equation for the latter change is shown below.



Zinc oxide is used as a white pigment in paints. It has the advantage over the commonly used basic lead carbonate (white lead) that it does not darken when hydrogen sulfide reacts with it, i.e., zinc sulfide is white while lead sulfide is black. Zinc oxide is also employed in large quantities as a filler in rubber articles. Ointments sometimes contain it as a germicidal substance.

Zinc chloride is prepared by the action of hydrochloric acid upon metallic zinc, the oxide or carbonate. Thus, in the case of the latter:



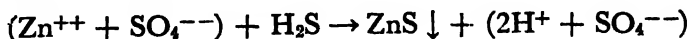
This salt is used as a wood preservative. Zinc chloride solution is forced into wood pores under pressure, where it discourages bacteria, fungi, termites, etc. Zinc chloride is also used, along with ammonium chloride, as a cleaning agent in the soldering of tin surfaces. Its function is to dissolve metal oxides and so keep the surface clean and insure good adhesion of the solder.

Zinc sulfate is prepared by careful roasting of sphalerite.



The salt is then separated from insoluble impurities by dissolving with water (leaching). It crystallizes as the heptahydrate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, known as *white vitriol*. It is used in the manufacture of paint pigments, as a mordant in dyeing, and in medicine.

Zinc sulfide is prepared by the action of hydrogen sulfide on zinc sulfate solution.



It is used as a white pigment in paints and as a filler in rubber.

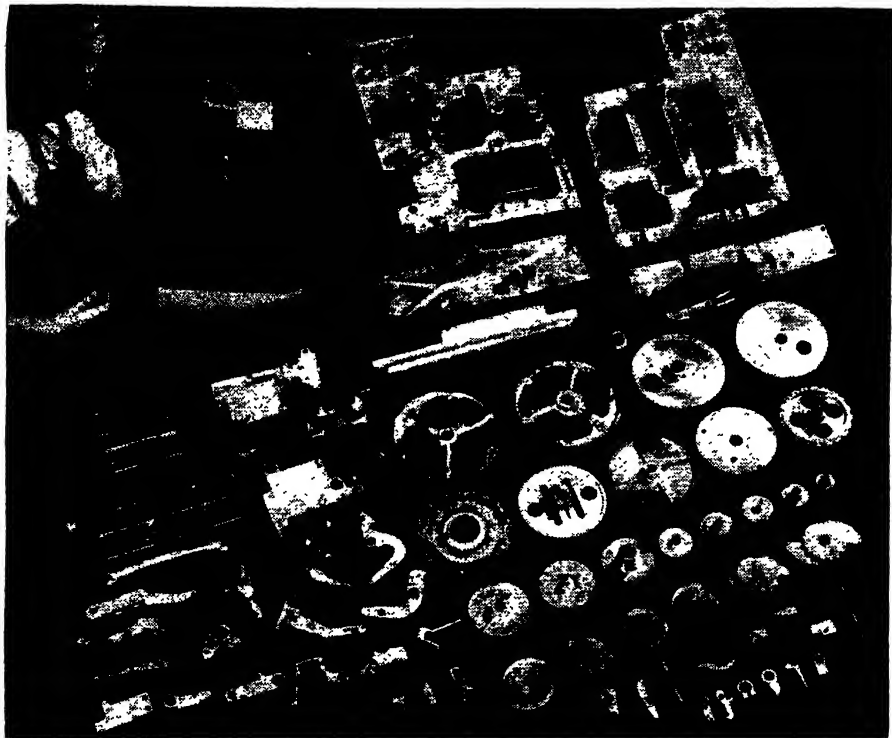
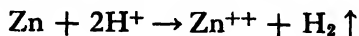


FIGURE 11.8. Zinc Die Castings. These are all parts used in a time recorder. Courtesy American Zinc Institute.

Uses of Zinc. The chief use of zinc is to protect the surface of iron articles from corrosion. Many metal articles are preferably made of iron because of the cheapness and strength of this substance, but protection against rusting is then required. One way of doing this is to coat with zinc, either by dipping the article in molten zinc, electroplating, spraying with molten zinc, or heating articles after dipping them in zinc powder. Galvanized (molten zinc) or sherardized (zinc powder) objects result.

The second largest use for zinc is in the die casting industry where zinc alloys, such as those containing small amounts of aluminum, magnesium, and perhaps copper, are used. *Brass* is another familiar alloy of (chiefly) copper and zinc. Zinc is also used as the negative electrode of batteries and in the preparation of hydrogen in the chemistry laboratory.

Metal Couples. When pure zinc dissolves in, say, hydrochloric acid, the fundamental change which takes place is a displacement. Zinc atoms give their electrons to hydrogen ions, converting the latter into hydrogen atoms. These then combine in pairs to form hydrogen gas molecules.



If a piece of copper is put in the same solution in contact with the zinc, or is connected to it with a wire, a change becomes apparent. Hydrogen gas now comes off from the copper, although the zinc continues to dissolve. The explanation is that as zinc atoms change to zinc ions in dissolving, the electrons left behind go to the copper, and are preferentially taken there by hydrogen ions, hence hydrogen gas forms at the copper surface.

Speaking in general terms, when a pair of metals are in contact in the presence of an acid or other electrolyte solution, sometimes even in very dilute solutions, *the metal higher in the activity series forms ions and sends electrons to the less active metal.* These ions do not always go into solution like the zinc ions above. They may react with anions such as carbonate or hydroxide ions to form insoluble substances which coat the metal. The coating may be tightly adhering and so prevent further action, or it may be porous and nonprotective. In general, then, the metal higher in the activity series either dissolves or corrodes to form insoluble corrosion products. Combinations of two metals which may act in this way are called *metal couples*.

General Changes in Metal Couples; Examples. In general, three changes occur when metal couples come in contact ^{in electrolyte solutions} (with) electrolyte solutions. (a) The most active metal forms ions, dissolving or corroding as described above. (b) Electrons pass from the most active to the least active metal. (c) Hydrogen gas may form, or other changes may take place at the surface of the inactive metal, because of the excess of electrons which accumulate there. There are several phenomena, familiar to the reader, which can be explained as being due to one or more of these processes.

A tin can consists of iron covered with a thin layer of tin. If the tin is scratched so that moisture comes in contact with the

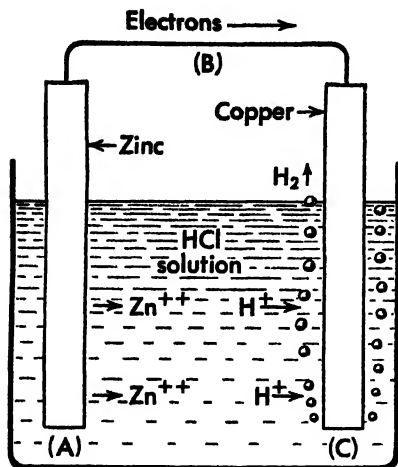


FIGURE 11.9. The Metal Couple Principle. (A) The most active metal forms ions, dissolving or corroding. (B) Electrons go from the most active to the least active metal. (C) Hydrogen is formed, or other changes occur at the surface of the least active metal as a consequence of the excess electrons there.

tin-iron couple the iron rusts, because it is higher in the activity series (i.e., is a more active metal) than tin. The rust is porous and does not protect the iron, hence the can rusts away rather rapidly in a moist atmosphere. On the other hand a galvanized container (iron covered with zinc) behaves differently. When damage exposes the iron, forming the iron-zinc couple, the zinc corrodes because of its greater activity. But a film of basic zinc carbonate forms and protects the zinc due to its tightly adhering nature. Corrosion therefore proceeds slowly, and a scratched galvanized object lasts much longer than a scratched tin can under conditions of equal humidity.

Another, modern application of the metal couple principle is the use of a magnesium bar in underfired hot water tanks used in the home. Magnesium, being well above both iron and zinc in the activity series, protects both of these metals by its presence. Iron or galvanized iron parts of water systems hence do not corrode, and "rusty" water from hot water faucets is prevented. The magnesium bar corrodes away in time, of course, and after several years must be replaced.

A use is made of the metal couple principle in the home, in the removal from silverware of the dark-colored film of silver sulfide which forms on the surface after contact with food containing sulfur compounds, such as eggs. The silverware is im-

mersed in a salt and soda solution in an aluminum container, causing formation of the silver-aluminum couple. As a result the aluminum corrodes slightly, it being much the more active

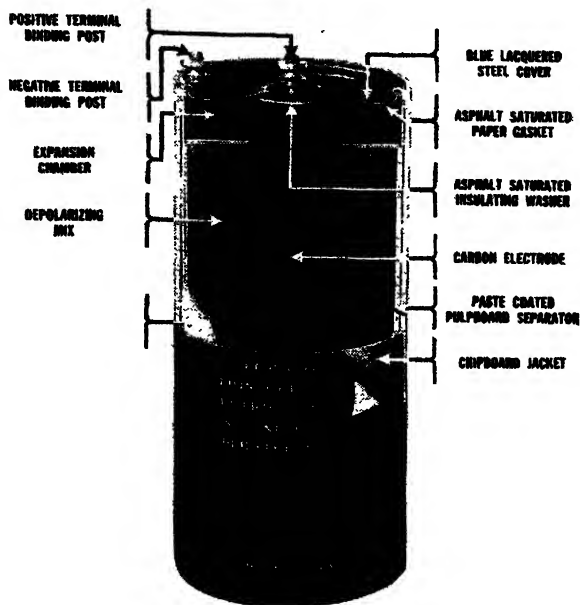
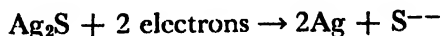


FIGURE 11.10. Cross Section of a Dry Cell.

metal, and excess electrons accumulate on the silver, causing sulfide ions to be given off from the silver sulfide film. The compound responsible for the discoloration is hence converted to metallic silver.



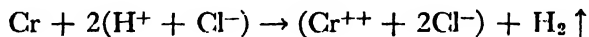
The electrons which travel from the active metal to the less active metal in a couple constitute an electric current, and metal couples in contact with electrolytes can therefore be used to generate electricity. This principle is widely used in the many "wet" and "dry" cells such as storage batteries, Daniell cells, dry cells, etc. Zinc and copper are used in the Daniell cell, but in most cells one member of the couple is not a metal. For example, lead and lead dioxide are the couple in the storage

battery, and zinc and manganese dioxide in contact with carbon are employed in dry cells. The latter are furthermore not actually dry, since they contain a paste of ammonium chloride and other substances with water. Couples used in this way as a source of electricity are connected with a wire only when generation of current is desired, since otherwise the cell would complete its chemical changes and would then be unable to supply further electricity.

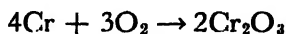
CHROMIUM

Occurrence and Metallurgy. Chromium occurs in the earth's crust chiefly as the mineral *chromite* ($\text{Fe}(\text{CrO}_2)_2$). The principal deposits of this substance are found in Rhodesia. Chromite is treated differently depending upon whether the metal chromium is desired or its compounds. If the metal is sought the ore is reduced with carbon, and an alloy of iron and chromium, known as ferrochrome, is the result. This is widely used in making chrom steels (see page 251). If chromium compounds are desired the chromite ore is heated with sodium carbonate in the presence of air, and water soluble sodium chromate is formed.

Properties. Some properties of chromium are given in the table on page 228. It is a hard, bluish-white metal used on automobile bumpers. Alloys of this metal are employed in making articles such as plumbing fixtures and cutlery. It dissolves in hydrochloric acid to form chromous chloride.



At high temperatures it burns to form chromic oxide, a stable green substance used as a pigment.



The pigment is not made commercially by burning the metal, however, but by reduction of chromates. The oxide dissolves with difficulty in acids to form chromic salts, such as chromic chloride (CrCl_3) and chromic sulfate ($\text{Cr}_2(\text{SO}_4)_3$). In hydrate form these

are green or violet compounds. They are commonly made by reduction of sodium chromate rather than from the oxide.

The chromates and dichromates are probably the most familiar chromium compounds. Yellow sodium chromate (Na_2CrO_4) is made by fusing chromite ore with sodium carbonate in the presence of air. It is converted to orange sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) with acids. The potassium salts K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ are also common laboratory chemicals.

Uses of Chromium and Its Compounds. The metal is widely used in electroplating of iron and steel, to give a hard, corrosion-resistant surface with a high luster. In the process a layer of copper is usually first electroplated on the iron, then a layer of nickel, and finally the chromium. Another important use for this metal is in alloys. Chromium added to iron gives a product with great hardness and strength, used in such places as armor plate and bank vaults. Iron alloys containing 12 per cent or more of chromium (stainless steel) are corrosion resistant, and find much use in cutlery. The wire generally used in electrical heating units is a nickel-chromium or a nickel-iron-chromium alloy (Chromel or Nichrome).

Chromium compounds are employed in the tanning of leather (chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), and as pigments (chrome yellow, PbCrO_4 , chrome green, Cr_2O_3). Chromic acid is used in chromium electroplating baths. The soluble dichromates are employed as oxidizing agents, as in *cleaning solution*, a mixture of sodium dichromate and sulfuric acid used to clean chemical glassware. Cleaning solution oxidizes the thin film of grease and dissolves other impurities present on glassware to give an unusually clean surface.

IRON

The Commonest Metal. When the word *metal* is mentioned, most people probably think of iron as a typical example, since this substance is by far our cheapest (page 228) and most widely used metal, and one sees on every hand common articles made



FIGURE 11.11. Open Pit Iron Ore Mining, Mesabe Range, Minnesota. Courtesy Republic Steel Corporation.

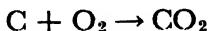
from it, such as nails, screws, tools, automobile engines and bodies, bridges, structural parts for buildings, etc. Iron is no newcomer in the field of metals. It has been employed for such a long time that no one knows when the first iron articles were made. It was used in many places thousands of years before the birth of Christ, and the world's early literature contains numerous references to iron objects, largely in connection with the waging of warfare.

Cost Factors. Three factors contribute to the cheapness of iron. (a) Iron compounds are common and plentiful in nature, since iron is the fourth most abundant element in the earth's crust, and many ore deposits are known. In this country the Lake Superior ore fields are the most important, in the states of Minnesota, Wisconsin, and Michigan. There are also extensive deposits in the vicinity of Birmingham, Ala. These are only the chief sources, however, and more than half of the remaining states have iron ore deposits rich enough to mine. (b) The ores of iron are relatively easily reduced to the metal, in a process requiring only

coke, air, and an inexpensive flux in addition to the ore. (c) Large-scale, economical methods have been worked out for reducing the ores. This is partly because iron ore reduction has been carried out for so many years that there has been time for extensive research on the subject.

Iron Ores. Small amounts of iron occur in metallic form in some rocks, but they are of no commercial importance. Iron is obtained chiefly from its oxide ores, *hematite* (Fe_2O_3), *limonite* ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), and *magnetite* (Fe_3O_4), and also from the carbonate *siderite* (FeCO_3). In this country hematite is the chief ore at the present time. In the metallurgy of iron and its alloys the reduction of the ore takes place in one step and the making of metal of the proper composition in another, while the formation of saleable articles requires still further metal working processes. Let us consider this metallurgy in greater detail, using hematite ore as the starting material.

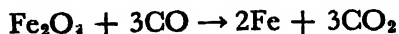
Metallurgy of Iron. The reduction of hematite is carried out in a tall, circular structure, about 100 feet high and 25 feet in diameter, known as a *blast furnace* (Figure 11.12). Iron oxide, coke, and a flux (usually limestone) are carried to the top of the blast furnace in special cars and put in at intervals, while pre-heated air is introduced near the bottom. As these substances move through the furnace a number of chemical changes take place. Coke first burns as it combines with oxygen from the hot air entering the lower part of the furnace.



The product of this oxidation, carbon dioxide, reacts with more coke to yield carbon monoxide.



The carbon monoxide reduces the iron oxide to lower oxides of iron and finally to metallic iron. Writing the reduction in one step:



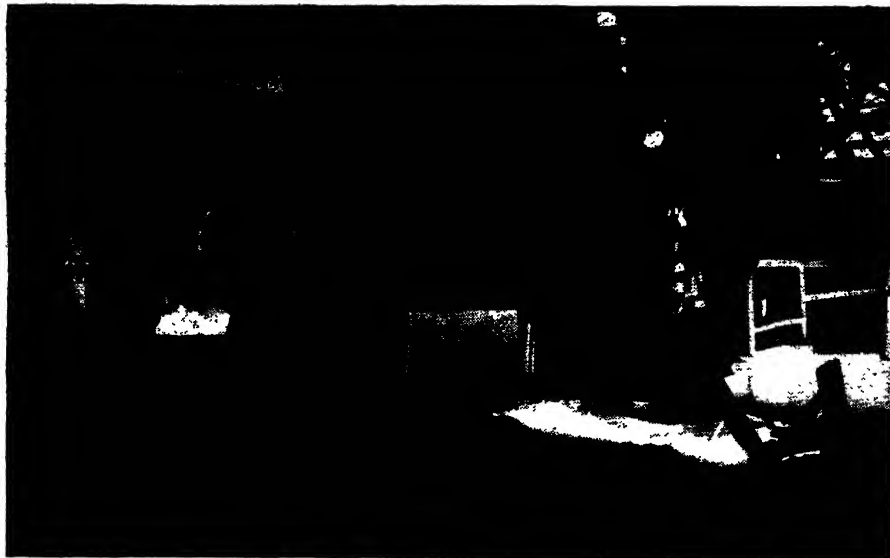
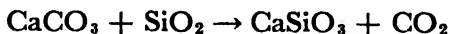


FIGURE 11.12. Tapping a Blast Furnace. Man in foreground is using an optical pyrometer to find the temperature of the molten iron. Courtesy Jones & Laughlin Steel Corporation.

The flux reacts with impurities in the ore to form a relatively low melting *slag*. The impurity is often silica and the flux calcium carbonate. The slag in this case is calcium silicate.



It is important during operation of the blast furnace that the contents be fluid, since the operation requires continuous movement of solids and liquids from top to bottom and of gases from bottom to top. This fluidity is insured in several ways; by pre-heating the air entering the furnace, by the heat of combustion of the carbon, by adding ingredients to form a low-melting slag and by the formation of an impure iron which melts about 300°C. below pure iron.

The molten iron goes to the bottom of the blast furnace, below the molten slag. It is drawn off from time to time as an impure product known as *pig iron*. This contains up to 5 per cent carbon and smaller amounts of silicon, phosphorus, sulfur, and manganese; it gets its name from the earlier custom of casting it into



FIGURE 11.13. Charging an Open Hearth Furnace. Courtesy Jones & Laughlin Steel Corporation, Otis Works, Cleveland.

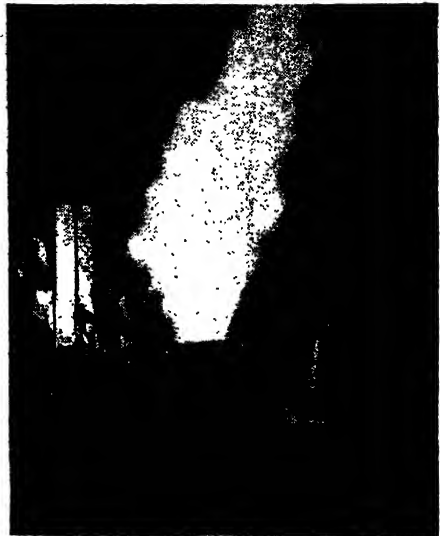


FIGURE 11.14. Bessemer Converter in Operation. Air blown through molten pig iron burns out impurities. Courtesy Republic Steel Corporation, Youngstown Works.

pieces known as “pigs.” Pig iron is not usable as such, because the impurities present make it brittle and lower its tensile strength. It is converted chiefly into many varieties of *steel*. On the average about 125 tons of pig iron are drawn from the blast furnace at a time.

The slag is also drawn off at intervals; about half as much of this material forms, by weight, as pig iron. The slag is not discarded, since it has a number of uses, chiefly as a substitute for crushed stone, as in road building and in concrete. Large amounts of gas are given off at the top of the blast furnace, about six tons for each ton of iron produced. This contains extra, combustible carbon monoxide, hence is used as a fuel, largely for preheating air which is about to be put into the bottom of the blast furnace.

Steel. Steel is not a definite chemical substance, but is the product made by treating pig iron, chiefly, in *Bessemer converters* (Figure 11.14) and *open hearth furnaces* (Figure 11.13). By far



FIGURE 11.15. Bar Mill. Courtesy Republic Steel Corporation, Massillon Plant.

the greater amount of our steel is now made by the open hearth process. The details of steel making are beyond the scope of this book, but in brief the carbon, phosphorus, sulfur, silicon, and other impurities present in the pig iron are largely burned out with air, or removed by a reaction with externally added slag-forming materials. Thereupon carefully measured amounts of carbon and alloy metals are added. A great number of different steels are made in this way, each having certain desirable properties as the result of its composition and heat treatment.

Properties of Iron. Some of the physical properties of iron are given on page 228. The properties of pure iron may be considerably changed when carbon or alloying metals are added to form products of industrial importance. Some of these changes are indicated in Table 11.3.

Iron Compounds and Their Uses. Iron has two common electrovalences, two and three. Iron atoms have two electrons in their outermost shell, and loss of these gives the *ferrous* ion,

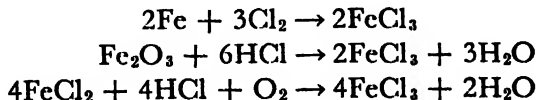
TABLE 11.3 Properties of Iron and Its Alloys

<i>Alloy</i>	<i>Approximate melting point</i>	<i>Approximate thermal expansion*</i>	<i>Approximate strength*</i>
PURE IRON	1535°C.	1.0	1.0
CAST IRON (3% carbon)	1200°	1	1
STAINLESS STEEL (Chrom-steel)	1500°	1	up to 5
INVAR (Nickel-iron)	1500°	0.07	2
ALLEGHENY METAL (Chrom-nickel steel)	1450°	1.5	1.8
DURIION (Silicon-iron)	1250°	1.3	0.3

* The thermal expansion and strength of pure iron have been called one. Values for the various alloys are then given relative to these.

Fe^{++} . Another, underlying electron can also be lost, resulting in the *ferric* ion, Fe^{+++} . In general, when metals exhibit two valences, the ending *ous* is used for the lower and *ic* for the higher. Besides ferrous and ferric compounds, for example, there are also chromous and chromic, cuprous and cupric, mercurous and mercuric, stannous and stannic, and others.

Ferric Chloride. Ferric chloride is the commonest soluble ferric compound. It is made by treating iron with chlorine, or ferric oxide or hydroxide with hydrochloric acid. It can also be made by oxidizing ferrous chloride in the presence of hydrochloric acid.



Ferric chloride is used as a mordant, this being a substance which causes dyes to adhere more firmly to cloth. The salt is believed to hydrolyze to ferric hydroxide which in turn clings to both cloth and dye (from Latin *mordere*, to bite). The combinations of mordants and dyes are known as *lakes*. These may vary in color if the same dye is used with different mordants, so another function

of the mordant is to produce certain shades of color with a given dye. Ferric chloride is utilized in medicine as a tonic, particularly in cases of anemia due to iron deficiency. It is also a blood coagulant, employed when severe bleeding must be stopped. The salt is commonly used in the laboratory when a solution containing ferric ion is required.

Ferrous Sulfate. The most important ferrous compound is the hydrated sulfate, green vitriol, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. This is prepared by action of sulfuric acid upon metallic iron. It is obtained in large amounts when sulfuric acid pickling fluid, used in cleaning iron surfaces, is evaporated. Green vitriol has been used to some extent like alum in water purification, where it behaves like aluminum sulfate (page 120). It is employed in the manufacture of dyes, in wood preservation, and in the making of iron inks. In the latter process ferrous sulfate and tannic acid are mixed in water solution. The weakly colored compound which forms is not satisfactory as an ink, but when it is put on paper and oxidized by the air, black, intensely colored ferric tannate results. To make the original ink colored so that it will be visible when being used for writing, a dye is added.

Iron forms a number of more complex compounds also, many of which are strongly colored. Examples are Prussian blue and Turnbull's blue, both thought to be $\text{KFeFe}(\text{CN})_6$, in which one iron atom is ferrous and the other is ferric. These are used as paint pigments. A much larger molecule containing iron is the red substance hemoglobin, with a molecular weight of about 63,000. This is a complex protein, present in red blood cells, which takes oxygen from the air in the lungs and transports it to all parts of the body for use in the exothermic oxidations of food molecules which furnish the energy necessary to sustain life.

TIN

Occurrence and Metallurgy. The metal tin has been known from ancient times. There is some question as to when tin was first prepared and recognized *by itself*, possibly about the time of the birth of Christ, possibly much earlier. But copper-tin

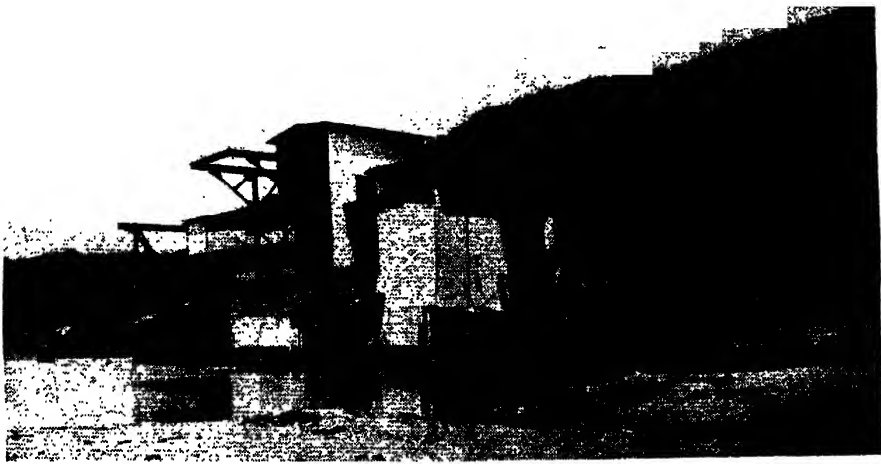
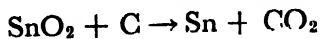


FIGURE 11.16. Dredging for Tin Ore in Malaya. Courtesy Tin Research Institute, Inc.

alloys (bronze) have been used since the early history of man. Bronze articles were made by the ancient Egyptians and Assyrians thousands of years before the Christian era.

Tin, like iron, occurs in minute amounts as the free metal. It is obtained commercially from the ore stannic oxide (*cassiterite*, SnO_2), named because in ancient times this ore was thought to have come from the Cassiterides, islands of uncertain location, but generally believed to be northwest of Spain. They may have been the British Isles, since Cornwall has since been the source of much cassiterite.

Most of the present-day tin comes from low-grade ores in Malaya, Indonesia, Bolivia, Belgian Congo, and Nigeria. The tin oxide ores are concentrated, then heated with powdered coal or other forms of carbon in reverberatory furnaces.



Tin is recovered in the molten state. The tin is purified in various ways, the most modern being by electrolysis.

This country has no tin ore deposits of value. Some tin is obtained by smelting imported ores at Texas City. Several

thousand tons of tin are recovered annually by alkaline detinning of tin plate clippings and electrolysis.

Properties of Tin. Some properties of tin are given on page 228. It is a silvery metal with a whiter cast than most metals. It is not hard, and it is used because of its chemical inertness to air and water rather than because of its strength. Tin exists in two allotropic modifications, i.e., two different forms in the same (solid) state. These are gray tin (density 5.75) and the ordinary white malleable tin (density 7.30). The former is stable below $13.2^{\circ}\text{C}.$ ³ and the latter above this temperature. The transformation from the relatively heavy white tin to the much lighter gray tin results in an expansion which in turn causes disintegration of the metal to a coarse powder. Back in the days when this phenomenon was not understood, it was called "tin pest" or "museum disease" because museum objects made of tin sometimes transformed to gray tin. Very small amounts of impurities in present-day commercial tin either retard the change very markedly or prevent it altogether, and instances of transformation to gray tin are now exceedingly rare. Another characteristic of tin is the sound it produces when a bar of the metal in the malleable form is bent. The crystals slip over one another, producing what is known as the "cry" of tin.

Compounds of Tin; Uses. Tin, like iron, forms two series of compounds, *stannous* (Sn^{++}) and *stannic* (Sn^{++++}). The most important compound in each series is the chloride. Stannous chloride is produced by the action of hydrochloric acid upon tin. It crystallizes from solution as the colorless hydrate, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The solution is used in the chemistry laboratory as a reducing agent, because of its tendency to pass to the stannic state. Stannic chloride is made by the action of chlorine upon tin. In the anhydrous form it is a liquid, but from solution crystals of the colorless pentahydrate form, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. Both chlorides are used as mordants and in the weighting of silk.

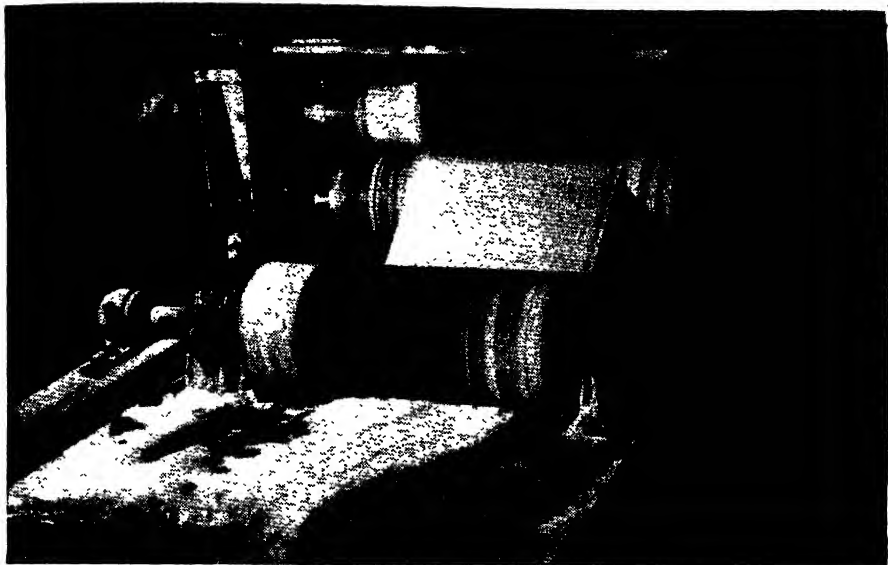
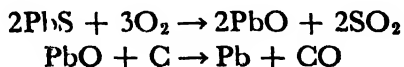


FIGURE 11.17. Making Tinplate by Electrolytic Deposition of Tin. Courtesy Weirton Steel Company.

Metallic tin is used as a protective coating for iron in the familiar tin can. It is also employed in various alloys. These include bronze (copper-tin), pewter and solder (lead-tin), and bearing metal (tin-antimony-copper). Other metals may also be present in these alloys in smaller amounts, as shown in Appendix C.

LEAD

Occurrence and Metallurgy. Lead is another metal known from early times, and lead objects were used by the Egyptians and Babylonians long before the birth of Christ. The metal occurs chiefly as the sulfide (*galena*, PbS). The obtaining of lead from its ores is somewhat more complex than in the case of many of the metals. If the sulfide is the starting product this is crushed and concentrated, then reduced in a series of reactions involving partial roasting, addition of iron oxide, carbon, and limestone. The simplest pair of reactions are shown by the following equations:



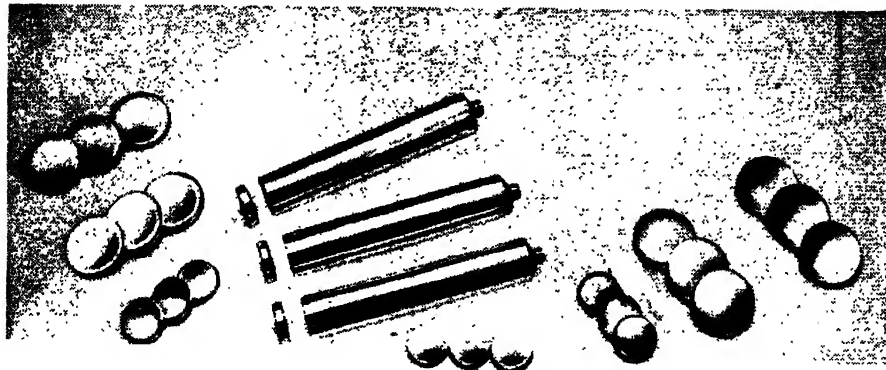


FIGURE 11.18. Tin-Coated Lead Blanks. Collapsible tubes for tooth paste, shaving cream, etc., are punched from these. Courtesy National Lead Company.

The metallurgy is complicated by the fact that enough silver and gold are often present in the lead to make the recovery of these metals profitable. One prominent method of separating these metals from the lead is by electrolysis. A bath of fluosilicic acid (H_2SiF_6) and lead fluosilicate (PbSiF_6) is used. Impure lead anodes go into solution and the lead plates out on pure lead



FIGURE 11.19. Naturally Occurring Lead Sulfide (Galena). Courtesy Ward's Natural Science Establishment, Inc.



FIGURE 11.20. Mining Lead Ore. Courtesy Eagle-Picher Mining & Smelting Company.

cathodes. Part of the impurities, higher in the activity series than lead (iron, zinc, chiefly), stay in solution in this process. The other part, lower in the activity series (chiefly gold, silver, bismuth), drops from the anode during the electrolysis and becomes part of a sediment, known as anode mud, which forms below this electrode.

Properties and Uses of Lead. Some properties of lead are given on page 228. The metal is soft and lustrous, but quickly becomes dull when exposed to the air because of the formation of a basic carbonate-oxide coating on the surface. The metal is not as commonly used around the home as those already described, because of its softness and the toxicity of its compounds. However, it is employed in storage batteries, waste pipes, electric cable sheaths, and in the solder used on tin cans. It is not as good a conductor of electricity as many other metals. It has a conductance only about one thirteenth that of copper when wires of equal diameter are compared, and still less when equal weights of wire are compared.

Lead Compounds. Lead has four electrons in its outermost shell (more than most metals). It forms a few compounds in

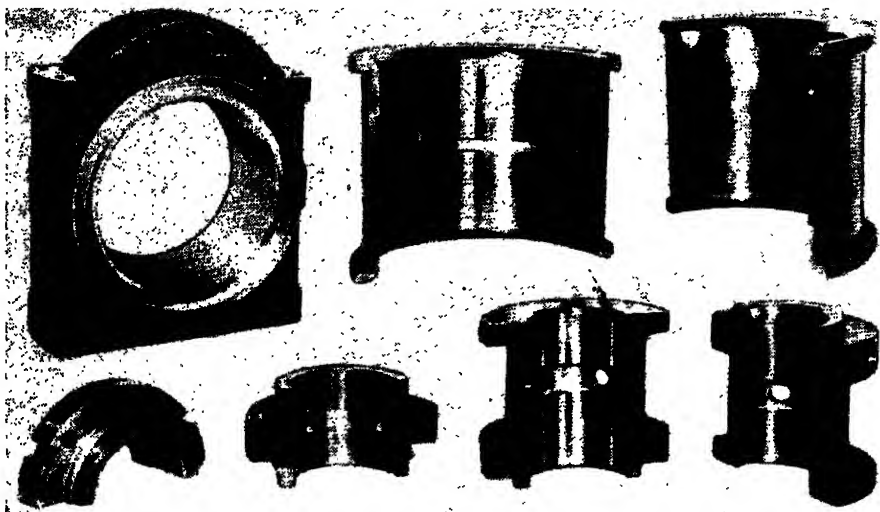
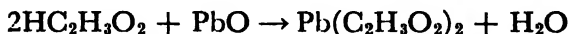


FIGURE 11.21. Babbitt-Lined Bearings. Babbitt contains hard crystals of antimony in a softer matrix containing one or more of the metals copper, tin, lead. The load is borne chiefly by the hard crystals. Courtesy National Lead Company.

which a valence of four is exhibited, such as lead dioxide and tetraethyl lead, but the more important valence is two, indicating that two of its outer electrons are more readily lost than the remaining two. Lead forms several oxides, the commonest being *litharge* (PbO) and *red lead* (Pb_3O_4). The former is used in making lead salts, chiefly the nitrate and acetate, by action of the appropriate acid. Thus, acetic acid and lead oxide give lead acetate and water.



Red lead is used as a pigment in paints. Lead dioxide (PbO_2) is a brown substance which is present at the positive terminal of a charged storage battery. Two other compounds of lead are important as paint pigments, the yellow chromate (PbCrO_4) and the white basic carbonate (*white lead*, $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$).

Soluble lead compounds are toxic. The effect is somewhat cumulative because of the slow elimination of lead from the body once it has been assimilated. Lead absorption by the body

occurs when soluble compounds of the metal are taken in either through the stomach or the lungs, and great care must be observed by workers in industries employing such compounds.



FIGURE 11.22. Native Copper from Keweenaw Peninsula, Michigan. Courtesy Ward's Natural Science Establishment, Inc.

C O P P E R

Occurrence and Metallurgy. This is another of the ancient metals, known and used thousands of years before the Christian era. The copper-tin alloy, *bronze*, was the earliest employed by man, and ancient metal objects made of nearly pure copper have also been found. The name copper has come about by corruption of the word Cyprus. In the days of the Greeks and the Romans the island of Cyprus was one of the chief sources of copper ores. The name of the metal from Cyprus changed through the years to such forms as cyprium, cuprum, copper (English), and kupfer (German).

Copper occurs as the free metal in some regions in sufficient quantities to make the mining of this form profitable, as in Michigan, for example. However, most copper is obtained from its compounds, chiefly sulfide ores in which the metal is associated with iron, arsenic, or antimony. The metallurgy of these ores is complex, and lies outside the scope of this book, but in brief the ground ore is concentrated (Figure 11.23) and then smelted



FIGURE 11.23. Concentration of Copper Ore by Froth Flotation. Low quality ore is mixed with water and small amounts of certain oils. A froth of high-grade copper ore, oil, and air rises to the top. Courtesy Anaconda Copper Mining Company.

in such a way that iron is converted to a silicate slag and copper is obtained by a reaction between cuprous oxide and cuprous sulfide, both of which are formed during the smelting.



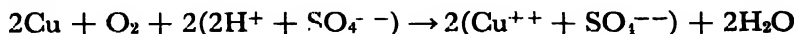
The impure copper obtained in this way is usually electrolyzed to obtain the pure metal. The anode mud from the electrolysis is sometimes rich enough in gold and silver to pay for the process.

Properties and Uses of Copper. Some properties of copper are given on page 228. The metal is valuable because of its malleability and ductility, and because of its excellent heat and electrical conductance. It is also less easily corroded than many metals, although moist air causes formation of a green basic carbonate, *verdigris*, on its surface. Copper is used in many important alloys, such as *brass*, the chief components of which are copper and zinc; *bronze* (copper-tin); *Monel metal* (copper-nickel); *German silver* (copper-zinc-nickel). In the home copper is used chiefly in wire form, to conduct electricity, and

in alloys found throughout the home, as doorknobs, screws, switchplates, plumbing, coins, fireplace accessories, and some cooking utensils. German silver is commonly used as a base metal underneath the silver in plated silverware. In spite of the name of this alloy, it contains no silver (see above).

Copper Compounds. Copper atoms have but one electron in the outermost orbit, and an electrovalence of one when this is lost (cuprous copper). A second, underlying electron is also readily lost, however, giving a second series of copper compounds in which the electrovalence is two (cupric compounds). These are of greater importance than the cuprous compounds.

The chief soluble compound of copper is hydrated cupric sulfate, *blue vitriol* ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). The latter is prepared by treating copper with sulfuric acid. Air must be present if the acid is dilute.

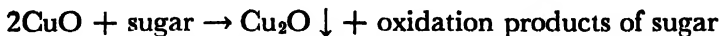


Cupric sulfate is also prepared by treatment of cupric oxide with sulfuric acid, and by partial oxidation of cupric sulfide. It may be made, too, in displacement reactions. The salt is used in solution for the electroplating of copper, in certain types of batteries, and in general wherever a soluble copper compound is required. One interesting use is to prevent algae multiplication in water. When these organisms are present in sufficient number in drinking water they cause disagreeable odors and tastes. But they are very sensitive to copper ions, which prevent the growth of most species in concentrations as low as two or three parts per ten million parts of water. Copper sulfate is also used in the preparation of Fehling's and Benedict's solutions, employed for the

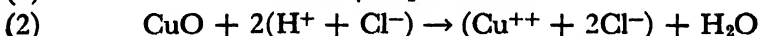


FIGURE 11.24. Hydrated Cupric Sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. These crystals are blue in color.

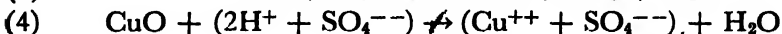
detection of reducing sugars (page 369) in urine. In preparing these solutions the copper sulfate is converted to what can be regarded for simplicity as a suspension of blue, hydrous cupric oxide in water. This is changed by reducing sugars (usually glucose) to red, insoluble cuprous oxide. The latter is observed at once by its color and the fact that it precipitates.



Oxidation-Reduction Equations. Copper is the first metal studied which is *below* hydrogen in the activity series. This means that hydrogen will not be displaced by the action of, say, hydrochloric acid upon copper. However, a chemical change will still take place if oxygen is present, i.e., the copper will react with the oxygen to form cupric oxide and this in turn will react with hydrochloric acid to form cupric chloride and water. The oxygen may be free, as in the air.



Or it may come from an oxidizing agent, such as concentrated sulfuric acid.



The cupric oxide formed in (1) and (3) is not apparent when one examines the reaction mixture, probably because it reacts immediately, upon formation, with the acid present to yield the ions of cupric chloride or sulfate. Actually, of course, we are sure only of the fundamental change from metallic copper to cupric ion, and the intermediate reactions above are merely how we imagine this change takes place. The true mechanism may be something different. Equations (3) and (4) can be combined into one equation which shows the starting and final substances without attempting to give a mechanism.



or, ionically:



Mercuric chloride (*bichloride of mercury*, HgCl_2) is a soluble, highly poisonous salt (all soluble mercury compounds are toxic). It is prepared by direct action of chlorine upon mercury. It sublimes readily, and this property, together with its poisonous nature, accounts for the name *corrosive sublimate*, sometimes used. Another soluble compound, mercuric nitrate, is prepared by the action of excess nitric acid upon the metal. Mercuric fulminate ($\text{Hg}(\text{OCN})_2$) explodes when struck, and hence finds use as a detonator. It is made by treating mercury with nitric acid and alcohol.

SILVER

Occurrence and Metallurgy.

Metallic silver was probably known and used prior to 2500 B.C. It was called *argentum* by the Romans (meaning "the white metal"), and this name is the basis for the symbol Ag in use at the present time. When alchemy became popular, after the fall of the Roman empire, silver was called "Luna," from the moon, and a crescent moon was employed as a symbol. This accounts for the name *'unar caustic* which is still in use to some extent for molded silver nitrate. At one time in antiquity silver was regarded as a more precious metal than gold.

The metal occurs in nature in the free state, and also in combination as the sulfide, the chloride, and in association with various copper and lead ores. Most of our silver now comes from these ores and is obtained during the electrolytic refining of the two metals. Mexico is the world's chief producer of silver.



FIGURE 11.25. Silver Crystallized on Native Copper. Houghton County, Michigan. Courtesy Ward's Natural Science Establishment, Inc.

Properties and Uses of Silver. Some properties of silver are given in the table on page 228. Silver owes its popularity to its bright luster, its excellent malleability and ductility, its high position among the metals as a conductor of heat and electricity, and its chemical inertness. It is not corroded by air or water. However, many sulfur compounds react with it to yield black silver sulfide, and this is the cause of the tarnish which commonly appears upon silverware in the home.

The metal is used in making cutlery and certain food containers, such as pitchers and sugar bowls, and as a plated metal upon these. It is also employed in coins and jewelry. Pure silver is too soft for this purpose; to make it harder it is usually alloyed with copper. Jewelry and coin silver is often an alloy consisting of about 90 per cent silver and 10 per cent copper. Silver solder is a silver-copper-zinc alloy which may also contain tin.

Compounds of Silver. The most important compounds of silver are the nitrate, chloride, and bromide. Silver nitrate is made by the action of nitric acid upon silver. Since silver is below hydrogen in the activity series and nitric acid is an oxidizing agent, no hydrogen is evolved.



Silver is oxidized and converted to an ion in the same general manner as copper (equation, page 262). Nitrogen dioxide gas is the reduction product of the nitric acid when the latter is used in strong concentration.

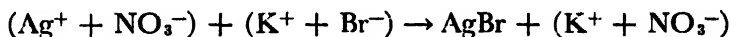
Silver nitrate is utilized chiefly in the precipitation of insoluble silver compounds, notably silver bromide, employed in photography (see below). It is also used as an ingredient in marking inks. Here, black metallic silver is precipitated on cloth as the result of the reduction by organic materials present. In finely divided form the metal appears black rather than silvery, as do many other metals. Black stains also form when silver nitrate solution is allowed to remain in contact with the skin, and for the same reason. Silver nitrate is used to cauterize wounds, and hence is

sometimes given the name which comes down to us from the past, lunar caustic.

Silver chloride and bromide are the most important insoluble compounds of silver. The former is universally used by chemists as a test for the chloride ion. A white precipitate, virtually insoluble in nitric acid, shows the presence of chloride ion when silver nitrate solution is added to the solution being tested. Silver chloride is also employed in the quantitative determination of both silver and chloride ion. Silver bromide is the chief active substance used in photography.

Photography. Silver chloride, bromide, and iodide are photo-sensitive substances, by which is meant they are decomposed by light. This can readily be observed in the laboratory with, say, precipitated silver chloride. Originally white, it soon turns purple when exposed to the light.

Of the three silver compounds, the bromide is most commonly used in photography. It is precipitated in the presence of gelatin by the reaction between a soluble bromide, such as potassium bromide, and silver nitrate.



The other product of the reaction, such as potassium nitrate, is washed out of the shredded gelatin gel, and the latter is then warmed to melting and spread over a film, commonly cellulose acetate or nitrate. The gelatin layer containing grains of silver bromide is known as the "emulsion." The silver bromide is kept dark, or exposed to no more than a dim red light, during its entire life, except for a brief instant when the picture is snapped.

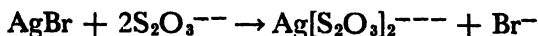
A camera is an optical system so designed that an accurate image of the scene being photographed is produced on the film when the shutter is opened. A few of the silver atoms in some of the silver bromide grains in the emulsion are reduced to metallic silver when light strikes these grains. However, these are so few that the change is not visible until the film has undergone further chemical treatment, in a process known as *developing*. The film



FIGURE 11.26. The Start of Film Making. A cellulose acetate or nitrate suspension is spread on a large wheel at the left of each machine. As the wheel rotates the suspension dries and is pulled off as a film which then moves from left to right in the machines shown. Solvent vapors are recovered here. The film continues down to the right and later receives the emulsion layer shown in Figure 11.27. Courtesy Eastman Kodak Company.

is put into a solution containing a mild organic reducing agent, commonly pyrogallol or hydroquinone. This first attacks the grains of silver bromide containing silver atoms as a result of light absorption. If the developing time is properly adjusted only these silver bromide grains are changed to metallic silver, and grains in which no light absorption took place are not affected. Eventually, however, if the film is left too long in the developer, all of the silver bromide will be reduced.

The film is next put into a sodium thiosulfate ("hypo") solution. This dissolves the unreduced silver bromide, forming a complex, soluble, silver thiosulfate ion, perhaps $\text{Ag}[\text{S}_2\text{O}_3]_2^{--}$.



The metallic silver from the reduced silver bromide grains is not affected by sodium thiosulfate solution. The metal does not have

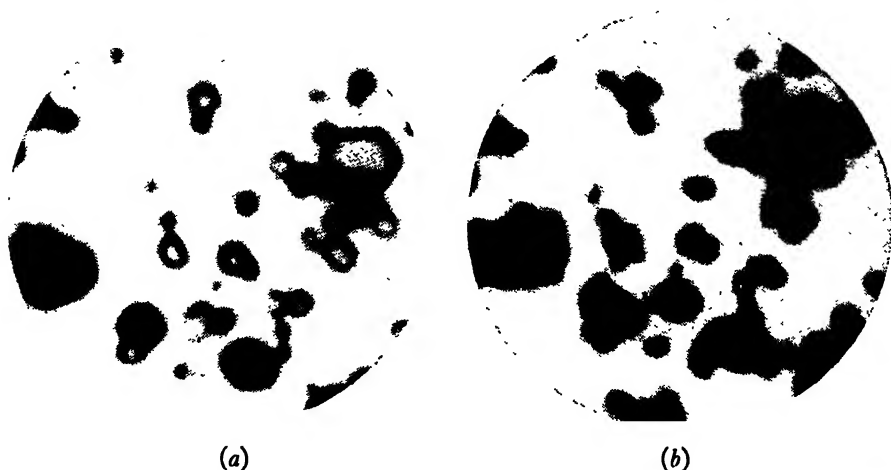


FIGURE 11.27. Photographic Emulsion. Magnified 5000 times, this shows (a) silver bromide crystals and (b) metallic silver from these crystals after exposure and development. Courtesy Eastman Kodak Company.

the shape of the grain from which it came, but forms an irregular filament (Fig. 11.28).

The emulsion layer on the film now consists of only gelatin and silver metal, and can be exposed to light, since all photo-sensitive silver bromide has been removed. The amount of metallic silver on any spot on the film, and therefore the amount of blackness, is proportional to the amount of light which hit that spot during the exposure. Hence there is a reversal of black and white on the developed film as compared to the scene originally photographed, and for this reason the film is called a negative. To make the final print, a second negative is made of the first negative, causing another reversal of black and white. The print therefore resembles the original scene in its light and dark contrasts. The print is generally made on opaque, white paper so that the white in the original scene will come out white on the picture, rather than transparent.

This has been an explanation of simple, black and white photography, but research has pushed the subject far beyond

this stage. Low energy radiation in the infrared can now be photographed, so that a picture can be taken by the heat of a warm object, such as a stove or an iron. Color photography is commonplace. Photographic processes are now available, too, in which the final print can be very quickly taken from the camera used to expose the film.



FIGURE 11.28. Electron Microscope Photograph of a Single Silver Grain from a Silver Bromide Crystal. The magnification is 50,000 diameters. Courtesy Eastman Kodak Company.

G O L D

Occurrence and Metallurgy. This regal metal may well have been the first used by man, since it occurs free in nature, and therefore required no complicated metallurgy, back in the early days of man's history. Gold is a scarce metal, estimated to be not higher than fortieth among the elements in

the order of abundance. This scarcity, together with its chemical inertness and physical properties, makes it an excellent substance to use as a standard of value. In spite of its scarcity, gold does occur in significant amounts in a few spots, and the search for these has lured many men into the wilderness. An outstanding example of such a spot was the fabulous Comstock lode in Nevada, which yielded about 11 million dollars' worth of gold in a few days.

Gold is found in quartz veins and in alluvial sands resulting from weathering and river action upon these. The earlier methods for obtaining gold were used on alluvial sands, and took advantage of the high density of the metal as compared to that of the sand. Prospectors "panned" the gold-bearing sand, meaning they agitated it with water in shallow pans. The sand was carried off first and the gold remained in the bottom of the pan.

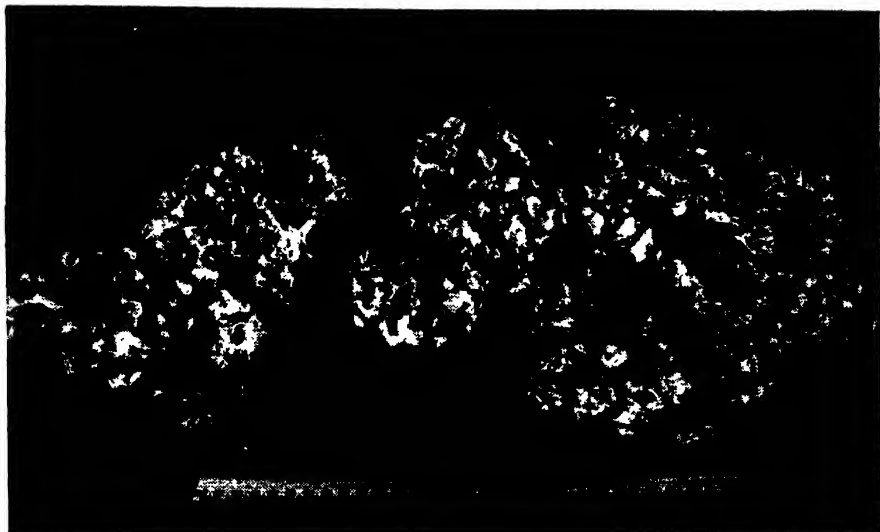


FIGURE 11.29. Gold. Replica of the “Welcome” nugget found in 1858 at Ballarat, Victoria, Australia. It weighed 2166 ounces. Courtesy Ward’s Natural Science Establishment, Inc.

The same principle is used in placer and hydraulic mining, but on a much larger scale.

Chemical methods were later used to recover gold, both from alluvial sands and from the crushed rock obtained from quartz veins. In these, the gold is separated from undesirable material in one of several ways, as (a) by amalgamating it with mercury, (b) by treating it with chlorine, or (c) by dissolving it in sodium cyanide solution in the presence of air. The chemistry of these processes will not be given here, but in each case metallic gold is efficiently removed from the sand or crushed quartz. Gold is found to some extent in combined form. The richest ore of this type is sylvanite, a gold-silver telluride. Gold is also obtained from the anode mud which accumulates during the electrolytic purification of copper, lead, and zinc. The refining of gold is now done chiefly by electrolysis. South Africa is the leading producer of the metal.

Properties and Uses of Gold. Gold is a remarkable metal. It is one of the most dense substances (19.3 g./ml.). A cubic foot

of gold therefore could not possibly be lifted by one man, since it would weigh in the neighborhood of 1200 pounds. One of the methods used in western stage coach days to prevent stealing of precious metals was to cast them into pieces of such weight that a holdup crew could not conveniently carry them off. Gold is our most malleable and ductile metal. It can be hammered and rolled into extremely thin sheets. The minimum thickness of these is uncertain, but some estimates have been as low as one millionth of a centimeter. This is approximately 100 angstroms, a distance which could accommodate only about 35 close-packed gold atoms. Sheets of gold of this order of thickness are translucent, and appear green by transmitted light. Gold is also so ductile that a cubic centimeter of it can be drawn into a wire over 50 miles long.

Gold has a characteristic yellow color, lighter than the color of the copper-gold alloys commonly seen in coins and jewelry. The purity of gold is expressed in carats, 24-carat gold being pure. A 12-carat ring, therefore, will be 50 per cent gold by weight, and the remainder will usually be copper, but silver, cadmium, nickel, iron, aluminum, and palladium are also used for alloying purposes.

Gold is used in coins, jewelry, various kinds of ornamental containers, dental work, and as gold leaf employed for lettering and decoration. Pure gold is too soft for most purposes; to harden it one of the alloying metals mentioned above is added, usually copper. Gold is not acted upon by air, water, or most other chemicals. Only soluble cyanides in the presence of air, chlorine, aqua regia (nitric and hydrochloric acids), and a few other substances attack it.

Self Study Questions

1. What general types of minerals constitute metallic ores? Give examples.
2. Give examples of a metal obtained from its ore by (a) electrolysis, (b) reduction with carbon, (c) displacement by another, cheaper metal, (d) heating in the air.

3. Give five physical properties which metals in general possess.
4. What is characteristic about (a) the number and (b) the binding force, in the case of the outer electrons of metal atoms?
5. What is meant by the activity series? Name several metals near the top and bottom of this series. Give an example of a displacement. Write the equation.
6. What is the evidence that the central part of the earth is metallic? Calculate the mass of the earth in kilograms, from the density (5.5 g./ml.) and the radius (4000 miles). *Answer:* 6×10^{27} g.
7. What are the principal ores of aluminum? Describe the metallurgy of this element. Give the important properties and uses of aluminum and its compounds. What is an alloy? Give an alloy of aluminum, and why it is superior to the pure metal. What is an alum? What gem forms of the oxide of aluminum are known?
8. In what two ways may metallic zinc be prepared from sphalerite? What are the important properties of zinc and its compounds? What two general uses does zinc have? What weight of zinc could be obtained by reduction of one ton of ZnO , assuming complete recovery?
9. Describe three changes which often take place when metal couples come in contact with electrolyte solutions. Give examples of changes of this sort which occur in the home.
10. What is the important ore of chromium? Describe how this ore is treated to obtain (a) chromium compounds, (b) metallic chromium. Describe the important properties and uses of chromium and its compounds.
11. Give names and formulas for several important ores of iron. What factors make iron the cheapest of all metals? How is pig iron prepared in the blast furnace? How is this further treated to make steel? Give the effect upon iron of adding carbon, aluminum, chromium, tungsten, silicon. Describe the preparation and uses of two important compounds of iron.
12. What is the important ore of tin? How is the metal prepared from this? Give the important properties and uses of tin and its compounds.
13. Give equations for two reactions which may take place in obtaining lead from galena. How is the metal purified? Give several properties and uses of lead and its compounds.
14. How is copper found in nature? Give several important properties of copper and its compounds. What are some of the uses of

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copper? What is blue vitriol? What weight of blue vitriol would be needed to insure one part per million of Cu^{++} ions in a billion liter lake?

15. What is the principal ore of mercury? How is metallic mercury obtained from this ore? Account for the symbol Hg. What property of mercury makes it of value in thermometers? In barometers? What are the two valences of mercury? Distinguish between calomel and corrosive sublimate.

16. Account for the symbol Ag for silver, and the name "lunar caustic" for silver nitrate. What is at present the chief source of our silver? What are three important compounds of silver? Give their preparation and uses. Start with silver bromide and go through the chemical changes involved in photography.

17. Describe how gold occurs and is obtained. What are the properties of this metal? How do we indicate the proportion of gold in jewelry? What metals are used in gold alloys? Calculate from the price (Table 11.1) the value of a liter of solid gold. Check the statement in the text that a cubic foot of gold weighs about 1200 lbs. If 50 miles of wire can be made from one cc. of gold, what is the diameter of this wire?

Answers: \$21,750; 0.0004 cm.

PART FOUR

Atoms with Unstable Nuclei; Atomic Energy

XII

Atoms with Unstable Nuclei; Atomic Energy

Not so very many years ago the nuclei of atoms would hardly have been considered of sufficient interest to warrant special mention in a book of this type. But it is now known that a tremendous store of potential energy lies in this part of the atom, and man is learning how to utilize it, for useful and destructive purposes. Controlled nuclear power, once a fiction writer's dream, is now so near reality that it will almost certainly have an important influence on the lives of many of the earth's present inhabitants. This subject has therefore become of vital interest to scientists and nonscientists alike.

Nothing has been said about atomic nuclei since the early part of the book. This is because the nucleus does not enter into the ordinary chemical changes which go on around us. These common, everyday processes have to do almost entirely with the outer parts of atoms—the electrons—which are continually shifting around as covalent or electrovalent compounds are formed or decomposed. In all of these changes the nucleus lies inert, beneath layers of electrons. We might never have learned of the possibilities lodged within this part of the atom but for the fact that a few rare elements in nature have atoms with unstable nuclei. When these disintegrate the effects produced are so unusual that scientists could not help but wonder about their cause. Our present knowledge of atomic nuclei began with the work which resulted from this curiosity. Let us consider briefly the early history of the subject.

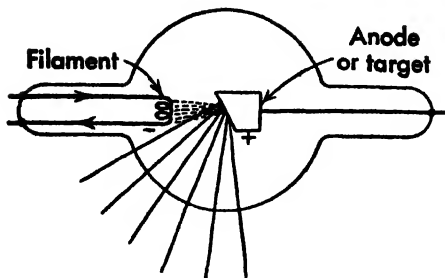


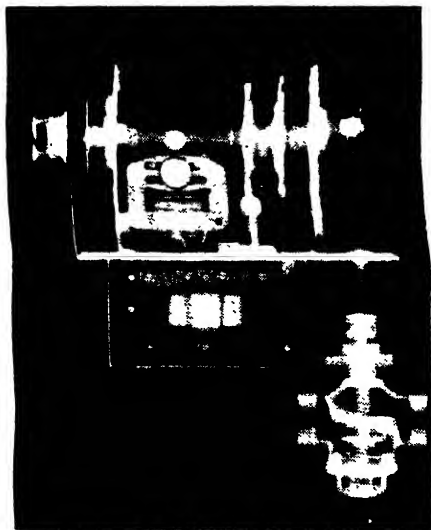
FIGURE 12.1. A Coolidge-Type X-Ray Tube. Electrons from a hot filament strike an anode at high speed causing the giving off of the very short-wave radiation we know as X-rays. From Ehret, et al., *Physical Science*. Copyright, 1942, by The Macmillan Company.

✓ **Early Years of Radioactivity.** In the year 1895 Roentgen (German) discovered how to produce the extremely powerful, short-wave radiation which we still know as "X-rays," after the name he used for them. He caused these rays to be formed by bombarding metal targets with a stream of electrons in an evacuated tube (Figure 12.1). The electron collisions with the target produced a host of

different radiations (page 54), among them being the penetrating X-rays. The latter caused some objects with which



(a)



(b)

FIGURE 12.2. High Voltage X-Ray. (a) A 2-million volt X-ray tube. This is inserted in the resonant transformer tank shown in the background during use. (b) Internal details of a motor-operated valve as revealed in a photograph taken by aid of this tube. High-voltage X-rays can penetrate a foot of steel and show up internal flaws. Courtesy General Electric X-Ray.

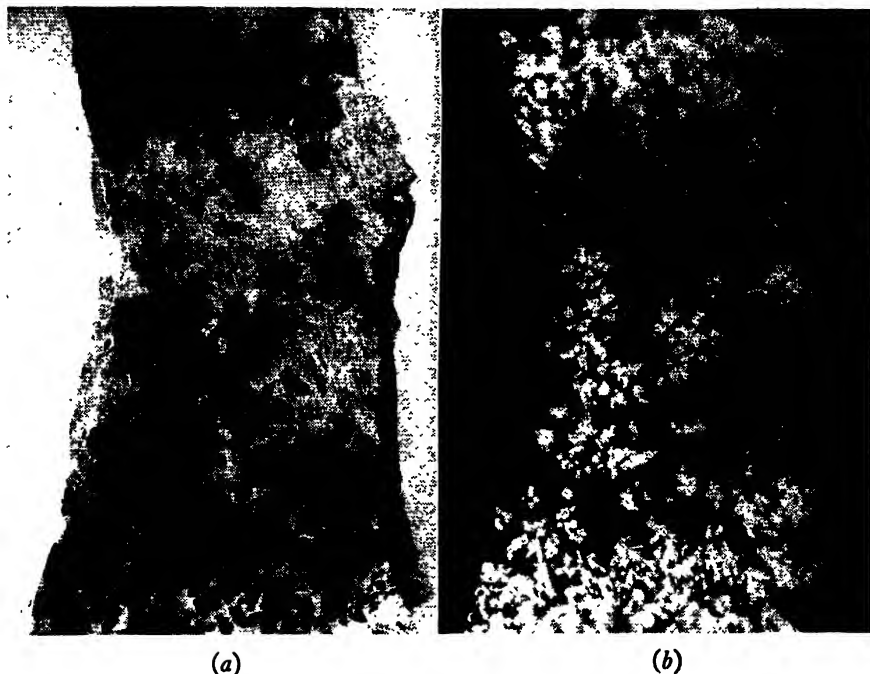


FIGURE 12.3. Uraninite, a Mineral Containing Uranium, Lead, and Thorium Oxides. (a) Photographed with ordinary light, (b) photographed with its own radioactive rays. Courtesy Ward's Natural Science Establishment, Inc.

they came in contact to give off visible light. The walls of X-ray tubes in operation, for example, were seen to glow brilliantly when made of certain types of glass. Photographic plates were also observed to be blackened by the X-rays, even though they were wrapped in black paper. The blackening of the film and the fluorescence were linked together, and scientists were stimulated to try experiments with other substances which were fluorescent or phosphorescent, i.e., which gave off "cold" light during or after excitation by X-rays or other radiation.

A prominent French physicist, Becquerel, found that the faintly phosphorescent substance potassium uranyl sulfate did affect a photographic plate, even through black paper and a sheet of metal. Subsequent experiments showed that all uranium compounds tested did likewise, whether or not they were phosphorescent (Figure 12.3). The scientists of that day did not know

it, but they were observing their first evidence of nuclear instability, or *radioactivity*.

If the effect upon photographic plates had remained the only way in which radioactivity could be studied, there would prob-

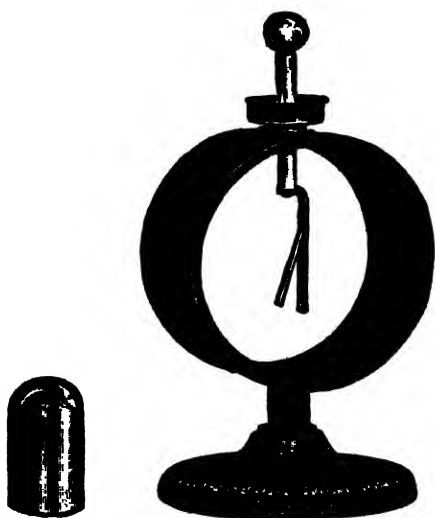


FIGURE 12.4. An Electroscope.

ably have been rather slow progress in the field. But Becquerel found a little later that uranium compounds also caused a more rapid discharge of a charged electroscope. The latter is an instrument which consists of a very thin, metal leaf fastened to a rod, as shown in Figure 12.4. The rod is connected to a metal knob outside of the container so that electricity can flow from one to the other. The whole is insulated from the container which protects the leaf by a plug of

some nonconducting substance, such as ebonite or sulfur.

If an ebonite rod is rubbed with a cloth, to give it a negative charge, and touched to the metal knob, the electrons which constitute the negative static charge on the rod leave in part and go to the electroscope. The leaf then moves out and assumes the position shown in the figure because it is charged similarly to the rod and is therefore repelled. The same thing happens when a positively charged glass rod is touched to the knob, but here the leaf, etc., becomes positively charged because of an excess of protons, since electrons have left the system to go to the glass rod.

Uranium compounds were found to discharge the electroscope at a more rapid rate than normally, as we now know because the emitted rays from the unstable nuclei ionized the air. The ions of opposite charge to the leaf were pulled to the latter and adsorbed, causing the charge on the leaf, etc., to be neutralized. Becquerel did not understand all this, but nevertheless he had

found a way of quantitatively studying radioactivity, because the more radioactive a substance was the faster it discharged the electroscope. Using this instrument a little later, Madame Curie and her husband were able to isolate compounds of polonium and radium—substances very much more radioactive than uranium itself—by making chemical separations and noting which part was the more radioactive, as shown by its effect upon the electroscope.

These more strongly radioactive substances made scientists intensely curious, because they exhibited properties different from anything observed up to that time, and even then suggested that they must come from a source of great power. Thus, radium salts were found to continually glow, even when in solution. They were always observed to be warmer than the surrounding air. They gave off powerful rays, some positively charged, others negative, as shown by the way in which they were turned in a magnetic field. Still other rays were given off which were not charged, since they did not bend in a magnetic field. The latter were found to have great penetrating power, and could easily pass through objects which were opaque to ordinary light. They are able to pass through as much as a foot of steel, for example.

For several years after the discovery of radioactivity the cause was not known. But in 1902 Rutherford and Soddy (English) made the very bold (at that time) suggestion that the phenomena were caused by the breaking up of atoms. Subsequent experiments have verified this suggestion, and from what we now know about the structure of atoms it appears rather certain that the part which actually breaks up and furnishes these radioactive effects is the nucleus.

✓ **Disintegration of Uranium.** Let us consider in the light of our present knowledge the radioactivity of uranium, without further historical background. The common *isotope* (page 32) in nature contains 92 protons and 146 neutrons in its nucleus. For some reason atoms with such a large number of protons and neutrons are unstable, and all of the elements with heavy nuclei from

polonium (atomic number 84) to californium (atomic number 98) are radioactive. The average life of a uranium atom is eight billion years, and since the earth is probably only about two or three billion years old it is clear that we still have the greater part of the uranium with which the earth started. The eight-billion-year life expectancy of uranium is an *average* value. Some uranium atoms break up long before this period has passed, while others will last far beyond it. It is like saying the average life expectancy of man is 65 years, but nevertheless some human beings die as babies and others live to be over 100. Accordingly, if one could observe a large group of uranium atoms at any moment during the present period of the earth's history he would see an occasional one of these decompose in what would be, to uranium, the teen ages or twenties of its existence.

In the disintegration which takes place, a small fraction of the uranium nucleus is thrown off, less than two per cent by weight. The portion emitted consists of two protons and two neutrons. This happens to be the nucleus of a helium atom, and it is also given the name *alpha* particle. It is positively charged as the result of containing two protons.

The unusual thing about this disintegration is the violence with which the alpha particle is thrown off. It erupts from the uranium nucleus with a velocity of thousands of miles per second, and is able to pass right through the atom's electrons, and through hundreds of thousands of *other atoms* before it is slowed down to normal molecular speeds. Great indeed must be the power locked up in a nucleus which can throw off a piece of itself with such vigor.

After losing two protons and two neutrons, the original uranium nucleus has changed in composition from 92 protons and 146 neutrons to 90 protons and 144 neutrons. With 90 protons, which means an atomic number of 90, the element is no longer uranium. It has become an isotope of the element thorium. This, in turn, is even more unstable than uranium, with an average life of only some 35 days. When its nucleus decomposes, furthermore, a different product is shot off—a tremendously speedy

electron, known to nuclear scientists as a *beta* particle. The latter leaves the nucleus many times faster even than the alpha particle just mentioned.

The beta particle, or electron, is believed to come from the disintegration of a neutron, within the nucleus, into a proton and an electron. The electron is emitted and the proton remains as part of the nucleus. When this type of disintegration takes place, then, the new nucleus formed contains one more proton and one less neutron than it previously had. The thorium isotope with 90 protons and 144 neutrons changes to an isotope of protoactinium, with 91 protons and 143 neutrons. But this in turn is so highly radioactive that it has an average life of only 1.65 minutes. This process of radioactive disintegration, or decay, as it is called, continues until *fourteen different changes have taken place*, whereupon a stable isotope of the element lead is formed, with 82 protons and 124 neutrons. These changes are shown in Table 12.1.

TABLE 12.1 Uranium Disintegration Series

<i>Element</i>	<i>Name used by nuclear scientists</i>	<i>Atomic weight</i>	<i>Average life</i>	<i>Particle emitted</i>
URANIUM	Uranium I	238	8×10^9 yrs.	alpha
THORIUM	Uranium X ₁	234	35.4 days	beta
PROTOACTINIUM	Uranium X ₂	234	1.65 minutes	beta
URANIUM	Uranium II	234	3×10^5 yrs.	alpha
THORIUM	Ionium	230	2×10^5 yrs.	alpha
RADIUM	Radium	226	2440 years	alpha
RADON	Radon	222	5.55 days	alpha
POLONIUM	Radium A	218	4.3 minutes	alpha
LEAD	Radium B	214	38.5 minutes	beta
BISMUTH	Radium C	214	28.1 minutes	beta
POLONIUM	Radium C'	214	10^{-6} second	alpha
LEAD	Radium D	210	24 years	beta
BISMUTH	Radium E	210	7.2 days	beta
POLONIUM	Radium F	210	196 days	alpha
LEAD	Radium G	206	stable	none

As the reader examines this disintegration series he will perhaps wonder at the repeated formation of elements like lead, bismuth, and polonium, in which they exhibit different stabilities after each formation. This is because different isotopes of these ele-

ments are formed each time, as can readily be seen by examining the atomic weights. Different isotopes of an element can differ very greatly in nuclear stability. The nuclear scientists have other names for the members of this and other series besides the element names. These are shown in the second column of Table 12.1.

Radium. The fifth change in this series produces the element radium, with an average life of 2440 years. This substance obviously disintegrates too rapidly to have existed from the start of our ancient earth. It occurs only because it is continually being formed from uranium. It exists only in association with uranium in nature, and is present to the extent of about one part per three million parts of the latter element. This ratio of one to three million is fixed by (a) the rate of decomposition of uranium, and (b) the rate of decomposition of radium. A rough analogy which may help make this clear is to say that in the manufacture of cigarettes from tobacco, the number of cigarettes existing in this country at the present time is fixed by (a) the rate of manufacture of cigarettes and (b) the rate at which they are being smoked. However, the cigarette-tobacco ratio is variable, affected by many factors, while the radium-uranium ratio is constant for all naturally occurring uranium ores.

Radium is recovered from uranium ores by a lengthy, multiple extraction method which is much the same as that used by the Curies. It is similar to the element barium in its chemical (not nuclear) properties. The price quoted at this writing (1952) by the United States Radium Corporation is \$20,000 per gram. The world's richest deposits of uranium ore are in the Belgian Congo. The richest deposits in North America appear to be in the region of Great Bear Lake in Canada. This is unfortunately in the arctic part of that country, far from industrial centers. Radium is used for medicinal purposes (chiefly for skin cancers), for industrial radiography (detecting flaws in metals by photographing the transmitted gamma rays), and has been employed in luminous paints. So many other radioactive isotopes are now

being prepared that the production of radium compounds may well decline in the future.

Types of Nuclear Decay in Nature. The subject of natural radioactivity may appear somewhat complicated to the reader at this point, but the following generalization may help. Naturally occurring radioactive substances in the earth's crust have nuclei which break up chiefly in two different ways.¹ (a) There is a loss of an alpha particle. Since this consists of two neutrons and two protons, each of which has a mass of one avogram, the atomic weight of the element drops by four avograms with this loss. The atomic number drops two, because two protons are lost with the alpha particle. (b) There is loss of a beta particle. This has such a small mass that no significant change in atomic weight takes place, but the process involves the breaking up of a neutron within the nucleus to yield the beta particle which escapes (an electron) and a proton which remains behind in the nucleus. The atomic number therefore increases one, because of the extra proton formed. These changes are accompanied in some instances by the giving off of powerful short wave radiation, called gamma rays, which are of shorter wave length and more powerful than ordinary X-rays. However, radiation can now be produced in an electron accelerator called a betatron which is more energetic than gamma rays.

It is apparent now why the particles or rays emitted by a sample of radium or other radioactive substance show three effects in a magnetic field. The positively charged alpha particles are turned in one direction, while the opposite bending takes place in the case of the negatively charged beta particles (electrons), and they are bent farther because their mass is so much less than that of alpha particles. The gamma rays, not charged, are unaffected by the magnetic field. This method of distinguishing between alpha, beta, and gamma emissions is illustrated in Figure 12.5.

¹ Other types of nuclear change occur in nature, but they are of minor importance.

The reader may wonder why beta particles are given off in the disintegration of radium, since according to the table on

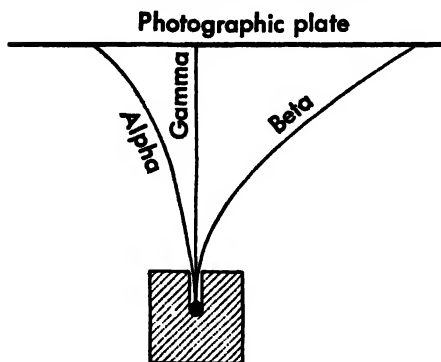


FIGURE 12.5. Effect of Magnetic Field upon Emissions from Radioactive Nuclei. Poles of the magnet are above and below the plane of the paper. Differences in paths cause three spots to appear on the developed photograph.

page 283 radium gives only an alpha particle. But a sample of radium or a radium compound has been disintegrating since its formation from uranium; hence there are also present the nine other elements formed from radium and shown in the table. Several of these emit beta particles when they disintegrate. A newly separated, purified sample of a radium salt would not give beta particles, but these would soon begin to ap-

appear as the disintegration products were formed.

The Age of the Earth. One interesting answer which scientists have found from the study of ancient uranium-bearing rocks is the age of these rocks, and from this it is possible to make a guess as to the probable age of the earth. It is seen from the table on page 283 that lead is the end product of the uranium disintegration series. We know how fast this is forming, from the study of the process as it goes on today. It is therefore possible to calculate, from the lead-uranium ratio of these rocks, how long the process must have been going on, i.e., the age of the rocks. The oldest rocks examined, from Karelia in Russia, have a lead-uranium ratio which indicates an age of about two billion years, but they are in contact with still older material which contains no uranium.

The present guess as to the earth's age is between two and three billion years. One factor which would make such a calculation erroneous would be the presence of ordinary lead in the uranium-bearing rocks at the start. But ordinary lead is a mixture

of isotopes with an average atomic weight of 207.21, while the lead formed from uranium is a single isotope with an atomic weight of 206. Modern analytical instruments readily separate the two kinds of lead and tell one from the other, and all rocks used for age determinations have been corrected for any ordinary lead present. As an independent check the alpha particles given off during the series of radioactive disintegrations can be determined, since they take on electrons and become ordinary helium gas. This is present in the rocks, and can be estimated. While results are low in some cases, undoubtedly because of diffusion of the gas out of the rock, nevertheless the ages of rocks found by this method are in fair agreement with those calculated from the lead-uranium ratios.

Considering the tremendous span of time involved, the two to three billion year estimate is not in great disagreement with the results obtained by other methods which have been used to calculate the earth's age. Thus, from the study of the rate of deposition of sedimentary rocks, and the best estimate of the total thickness laid down during the life of the earth, an age of about 1.3 billion years is obtained. However, the errors in this method are difficult to evaluate, and during the early part of the earth's life, surface temperatures may have been so high that no liquid water was available for forming sediments. Another method, based upon the braking effect of lunar tides, and the rate at which the moon is receding from the earth, gives a maximum age of this system of not over 4 billion years. It is also of interest to note that iron meteorites, not a part of the earth, have been found from helium analyses to have approximately the same age as the earth.

Other Disintegration Series. The disintegration series starting with uranium is not the only one known. The naturally occurring element thorium is also the parent of a decay series involving ten changes. The element actinium also heads a series, as do the transuranium elements neptunium, plutonium, americium, curium, berklium, and californium, with some duplication in their series.

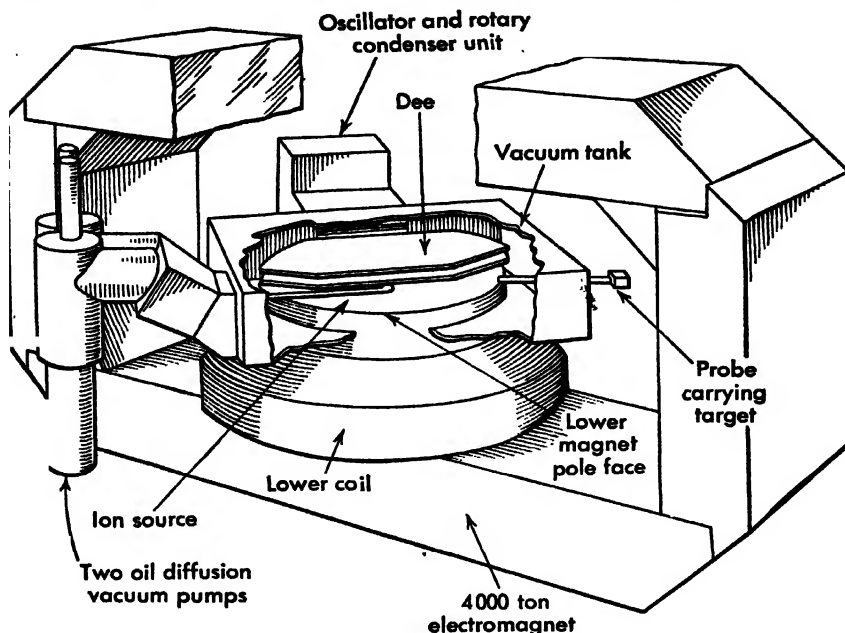


FIGURE 12.6. Cut-away Drawing Showing Parts of the Synchro-Cyclotron. Positively charged particles are spirally accelerated by two electrodes which rapidly change in sign (Dees) and by the turning force exerted by a large electromagnet. The synchro-cyclotron differs from the cyclotron in that a correction in pulse rate is made in the former to allow for the increase in mass of the positive particles which accompanies their increase in velocity. This leads to a beam of higher energy particles. Courtesy Radiation Laboratory, University of California.

ARTIFICIAL RADIOACTIVITY

In the year 1934 the Joliot-Curies (Professor Joliot and his wife, who is the daughter of Madame Curie) bombarded samples of boron and aluminum with alpha particles at the Radium Institute in Paris. These two elements were then found to have become radioactive, but the activity gradually declined in the period following the experiment. This was the first in a long and ever widening line of research in the artificial production of radioactivity which now includes such modern wonders as the uranium pile (page 300) and the cyclotron.

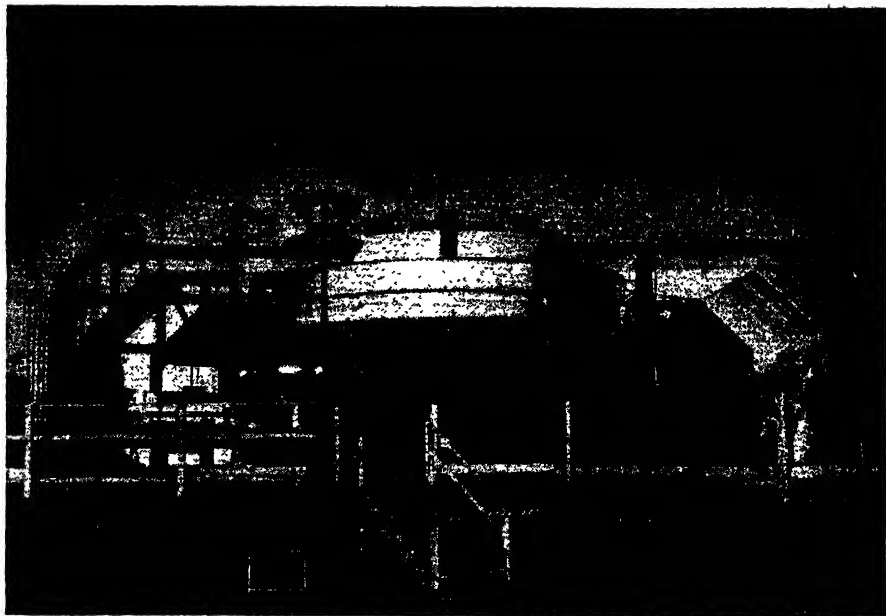


FIGURE 12.7. The 184-Inch Synchro-Cyclotron of the University of California. This is a view of the other side of the instrument shown in Figure 12.6. Courtesy Radiation Laboratory, University of California.

The Cyclotron. The cyclotron is a device for increasing the speed of positively charged particles² and controlling their direction so that a beam of these particles, moving at velocities up to 80,000 miles a second, can be made to collide with any substance which the investigator wishes to place in their path. If protons are the particles to be accelerated, hydrogen is ionized at the center of the cyclotron (Figure 12.6) to produce these. The protons are then caused to move outward in a spiral path at greater and greater speeds by subjecting them to two forces. The first is the turning force produced by a strong magnetic field, and the second an electrical force which reverses with high frequency so that the electrode or Dee which the proton is approaching is always negatively charged, producing a continuous series of electrostatic attractions which accelerates the protons. A powerful instrument of this kind is the 184-inch synchrocyclo-

² Protons, deuterons, tritons, alpha particles, and others.

tron at the University of California, with an accelerating force of about 200 million electron volts. Its proton beam is so energetic

that atoms of substances exposed to it may have their nuclei broken into several parts. Many radioactive nuclei are formed under these conditions.

The reader may wonder how these facts are known. The effects of such collisions can be observed in another modern device known as the cloud chamber (Figure 12.8). Clean air in a container is saturated with water vapor or other vapors and then supersaturated by expanding and cooling the air. Eventually the excess water will condense out on the sides of the container, but for a time it remains supersaturated. When β particles shot off during radioactive disintegration are allowed to pass through they ionize this air because of their high energy and charge. The water vapor then condenses on these ions, causing a visible line of fog to be formed (fog track) in the path of the particle (Figure 12.9). Collisions are shown by an abrupt change of direction of the fog track, or by the generation of two or more fog tracks if a nucleus is split. (See page 6.)

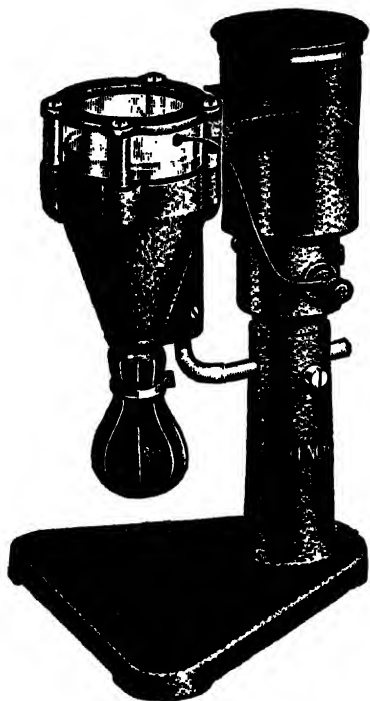


FIGURE 12.8. One Type of Cloud Chamber. The bulb is compressed and suddenly released, causing the air above to expand, cool, and hence become supersaturated with water vapor. Water then condenses on ions left as the result of passage of nuclear particles, making visible fog tracks. Courtesy Central Scientific Company.

In Figures 12.10 and 12.11 is shown another method of detecting high energy particles, by their effect upon photographic emulsions. A line of silver halide grains is affected, and after developing, photomicrographs can be taken of the path of the particle.



FIGURE 12.9. Cloud Chamber Photograph in a Magnetic Field. A meson is descending at the right and decaying with emission of an electron. An electron of lower energy is entering the chamber at the bottom, where the turning motion due to the magnetic field becomes more pronounced as the electron loses energy. Courtesy Brookhaven National Laboratory.

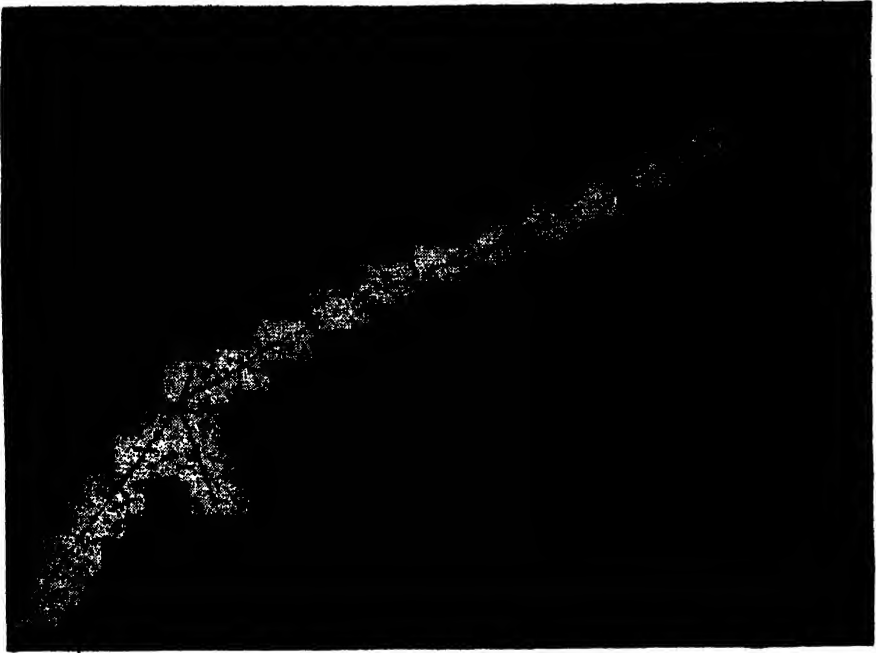


FIGURE 12.10. The Earliest and Most Recent Method of Showing Nuclear Changes—by Photography. Whereas in early experiments merely a blackening of the plate was produced, it is now possible to learn the paths of individual particles. In this illustration a negative heavy meson, entering from the upper right, has traveled through a pile of photographic films until it has struck an atomic nucleus. Several nuclear particles were ejected as the result of the collision. When the pile of films was developed, and photomicrographs of the tracks were spread out as shown, the paths of these particles became apparent. Courtesy Radiation Laboratory, University of California.

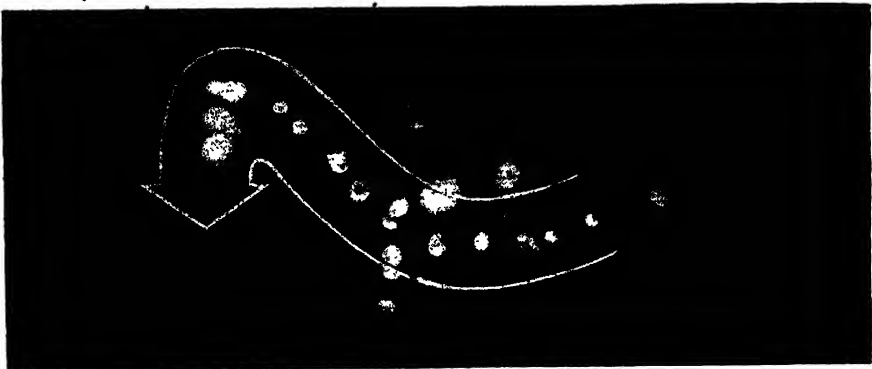


FIGURE 12.11. Path of an Electron. In this much-magnified picture of a photographic emulsion, the length of the track, 13 grains, is less than the thickness of an average sheet of paper. Courtesy Eastman Kodak Company.

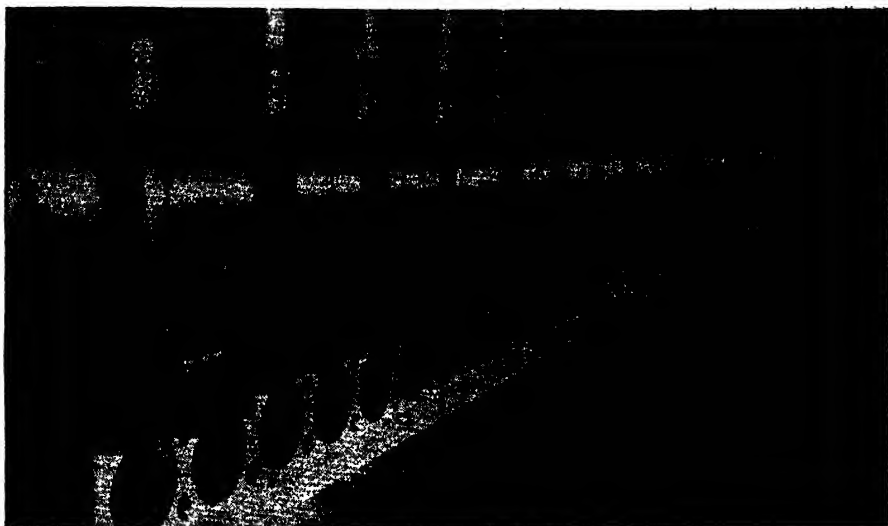


FIGURE 12.12. The Inside of a Linear Accelerator. Particles are accelerated electrically only when they are not shielded. During the time they are within the cylinders (drift tubes) the accelerating force is on its reverse cycle. Courtesy Atomic Energy Commission.

From the study of such results during recent years it has become apparent that in the case of very high energy collisions, new types of subatomic particles are produced, or perhaps set free, which have been given the name of *mesons*. These are of at least five different kinds, positive, negative, or neutral in character, and having different masses, but of the order of several tenths of an avogram. After being formed they disintegrate in a very short time, sometimes in as little as a few millionths of a second or less. Interest is high at the present time as to the role which mesons play in atomic nuclei, i.e., whether they exist as part of protons and neutrons and whether they have something to do with the binding force which holds atomic nuclei together.

Other types of particle accelerators are also in use, including the betatron, the synchrotron, and the linear accelerator; the latter accelerates particles in a straight line (Figure 12.12). A pilot model of the Bevatron is in use at the University of California (Figure 12.13).



FIGURE 12.13. Quarter-Scale Model of the Bevatron. This is a proton accelerator which, when built full scale, will produce particles with energies of several billion electron volts, hence the name BEVatron. The units beside the men are vacuum pumps. The ring-shaped magnet is also visible. Courtesy Radiation Laboratory, University of California.

Use of Artificial Radioactivity. Much information has been gained about atoms by the preparation and study of radioactive isotopes. It appears that of the 98 types of elements the first 83 have stable isotopes which are not radioactive, or at least do not have sufficient radioactivity to detect. But other isotopes of these 83 elements (and the remainder, for that matter) have been made, by the methods outlined above, or are otherwise known, which are lighter or heavier than the stable isotopes. These are radioactive, and it is by their preparation that the so-called

“artificial” radioactivity has been produced. In many cases, particularly among the elements with the smaller atomic numbers, the heavy radioactive isotopes—those with more neutrons than usual—go through the same beta particle type of disintegration found in some naturally occurring radioactive elements, while the isotopes with less neutrons than usual give off a new type of particle, the *positron*. This has the mass of an electron, but is positively charged, and it is sometimes referred to as a positive beta particle or positive electron. Positrons have an exceedingly short life, because when they meet an electron a mysterious process takes place in which both are annihilated, leaving nothing but two photons of radiation.

Radioactive isotopes are becoming of great importance in many lines of research because their presence can be detected, or “traced” by their radioactivity. This is made possible by the Geiger counter, a modern device as much superior to the electro-scope as that instrument was to the photographic plate (as it was originally used).

This is an electronic device for detecting the presence of charged particles active enough to penetrate an aluminum foil window, such as beta particles. These cause conductance of the air within the instrument to reach a threshold value and permit a surge of current which lights a light, rings a bell, or operates a counting mechanism or an oscillograph.

Radioactive substances can therefore be “followed,” even though they are out of sight, provided alpha or beta particles can get through whatever hides them to the counter. Thus, radioactive sodium in harmless amounts can be injected into the bloodstream and traced, and in this way a study can be made of the circulation of the blood. Complicated industrial processes can be analyzed. Radium and other radioactive substances, lost down drains and in sewers, can be found. The manner in which the elements move about in plants during their growth can be learned. A large, important field is developing in which radioactive isotopes of common elements not normally radioactive are employed to study processes of this type.

✓ TRANSMUTATION OF ELEMENTS

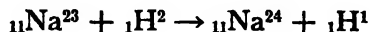
Thirty years ago, Rutherford (Lord Rutherford, director of the Cavendish Laboratory, Cambridge, England, who is now deceased) passed alpha particles through a specimen of nitrogen gas. When the experiment was completed the amazing (at that time) fact became clear that two elements, hydrogen and oxygen, were now present in the container with the nitrogen which had not been there at the start of the experiment. The only possible explanation for this was that the alpha particles (2 protons and 2 neutrons) had reacted with the nuclei of nitrogen atoms (7 protons and 7 neutrons), to form oxygen nuclei (8 protons and 9 neutrons) and hydrogen nuclei (1 proton). Thus for the first time man had brought about the transmutation of elements, and the alchemist's dream had come true. This, and the experiment of the Joliot-Curies described above, marked the beginning of a new branch of chemistry and physics, *that dealing with changes brought about by man in the composition of atomic nuclei*. Many more nuclear changes have now been caused to take place in this manner than are known to occur during the natural radioactive disintegrations which go on in the earth's crust.

Equations can be written for these nuclear changes just as for ordinary chemical changes. It is necessary to designate which isotope of a given element is taking part in such a change, since different isotopes may behave quite differently. The isotope is shown by writing the atomic weight after and a little above the symbol of the element. It is also customary to show the atomic number. It is written before the symbol, and a little below it. Thus, ordinary carbon has an atomic number of 6 (6 protons in the nucleus) and a mass of 12 avograms (sum of protons and neutrons is 12). In nuclear equations we therefore write:

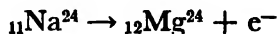


This shows nothing about the electrons surrounding the nucleus. Nuclear scientists ordinarily do not care whether an element is in the form of neutral atoms or ions, since their concern is only with the nucleus.

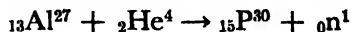
As examples of further transmutations can be given the effect of bombarding sodium atoms with deuterons. The radioactive sodium mentioned above is formed, together with ordinary hydrogen.



The nuclei of the ${}_{11}\text{Na}^{24}$ atoms are unstable and break down to form magnesium nuclei and electrons. This accounts for the radioactivity of ${}_{11}\text{Na}^{24}$.



As an example of a transmutation produced by alpha particles, consider the reaction between these and aluminum nuclei.



A neutron (${}_0n^1$) is given off each time a phosphorus atom is formed. This has an atomic number of zero and a mass of one avogram, and it is shown with a small "n" to distinguish it from nitrogen, although of course the zero charge and unit mass are identifications in themselves. The ${}_{15}\text{P}^{30}$ isotope is not stable. It breaks up in a peculiar manner to form a silicon isotope and a positively charged electron, called a *positron*.



It is not known how this is formed in the nucleus, but to account for the known change in atomic number it can be thought of as coming from a proton, which is then changed to a neutron in the process. Since a proton disappears and a neutron appears, the nuclear composition therefore changes from 15 protons and 15 neutrons to 14 protons and 16 neutrons, which is the nucleus ${}_{14}\text{Si}^{30}$.

These processes, and many more like them, involve the giving off of relatively small units from atomic nuclei, i.e., electrons, positrons, protons, and neutrons. The number of these small units given off by a disintegrating nucleus is also low, generally one. This seems to be the usual type of result when relatively slow-moving subatomic "bullets" are employed—relative, that is, to

speeds now attainable. But in recent experiments with the giant, 184-inch University of California cyclotron, using much more energetic subatomic particles, different, more spectacular results have been obtained. Some collisions have been of such violence that nuclei are observed to break into 20 or 30 pieces. Similar phenomena have been observed when particles from interplanetary space strike the earth's atmosphere.

A T O M I C E N E R G Y

Early Failures. The possibility of using nuclear changes as a source of energy has been recognized for a long time. The nucleus of an atom, hit by a subatomic particle, breaks up to form the nucleus of another atom and in so doing may liberate a great deal more energy than was required to fire the "bullet" which hit it. All readers of sufficient age probably remember the imaginative stories which used to appear describing the huge amount of energy that could be obtained in this way. But the practical difficulty which was always present in early experiments along this line was that of hitting the nuclei. So many bullets fired in the general direction of the target missed their mark because of the tininess of the nuclei, even compared to atoms, and the actual expenditure of energy in firing the subatomic particles was greater than the energy given off by the few disintegrating nuclei which were hit. For the same reason, too, the expense involved in transmuting inexpensive metals into precious metals was greater than the value of the metals obtained.

U-235. But in 1938, Enrico Fermi, working at the University of Rome, reported a new kind of nuclear change. He found that when the isotope of uranium, ${}_{92}\text{U}^{235}$, was bombarded with slow neutrons, an unusually energetic nuclear change took place. As the result of the work of Fermi and others, it was found that *three* phenomena occurred which were of the greatest interest and importance.

(1) The nucleus of this uranium isotope, instead of giving off small particles, as previous nuclei had done under bombardment

with subatomic particles, broke into large pieces, including nuclei of barium, krypton, xenon, and iodine. Many of these smaller nuclei were radioactive.

(2) Accompanying this disintegration was the emission of a number of *additional* neutrons. These caused other ${}_{92}\text{U}^{235}$ nuclei in the neighborhood to be hit and explode, and so on. The problem of poor marksmanship was thus overcome by the generation, during the nuclear disintegrations, of an increasingly larger number of neutron bullets. These also constitute one of the dangers in this type of nuclear decomposition (fission), because they are absorbed by various atoms in the human body (phosphorus, sodium, magnesium, etc.) which in turn become radioactive.

A process of this kind, where a change taking place in one atom liberates particles or energy which starts the same change in other atoms, followed by still others, etc., is called a *chain reaction*.

(3) A tremendous amount of energy was given off by each disintegrating atom, some 50 million times as much as is obtained by the burning of an atom of carbon, for example. This energy is largely absorbed by substances in the neighborhood of the nuclear change, causing a very great rise in temperature, perhaps by many millions of degrees when large numbers of ${}_{92}\text{U}^{235}$ nuclei are involved. The reason for this extraordinary emission of energy appears to be a loss of mass, i.e., the mass of all products of a material nature formed during the disintegration is less than the mass of the original uranium atoms. Our modern concept is that mass and energy are convertible, one into the other, the relation being that shown by the Einstein equation.

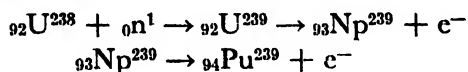
$$E = mc^2$$

E is the energy gained and m is the mass lost in a change of the type mentioned above. c is the velocity of light, and it is seen why a large gain in energy results from a tiny mass loss, because of the value of c , 3×10^{10} centimeters per second.

Plutonium. After the work on ${}_{92}\text{U}^{235}$, the element plutonium was prepared (Seaborg, American) and found to be fissionable

also. This element, furthermore, could be extracted more readily from the uranium pile, where it was made, than could ${}_{92}\text{U}^{235}$. At this writing plutonium appears to be the most promising source of atomic energy.

The uranium pile contains uranium chiefly as the nonfissionable isotope ${}_{92}\text{U}^{238}$, but a small amount of ${}_{92}\text{U}^{235}$ is also present, and this disintegrates upon neutron bombardment, giving other neutrons. It is these that activate the uranium pile. ${}_{92}\text{U}^{238}$ atoms pick up the neutrons, then change to neptunium which in turn becomes plutonium.



The fast neutrons liberated by disintegrating ${}_{92}\text{U}^{235}$ atoms are not readily picked up by other ${}_{92}\text{U}^{235}$ atoms. To perpetuate the chain which keeps the pile going they must be slowed down. This is accomplished by including graphite as part of the pile. Neutrons passing through graphite are not picked up, but lose speed to the point where they are absorbed by ${}_{92}\text{U}^{235}$ atoms.

Atomic Energy in Peace. Atomic energy for peaceful purposes is certainly possible, but at the present time it seems to suffer certain disadvantages from the standpoint of cost. It appears that small, mobile units for power generation are going to be difficult to make, and one estimate the writer has seen for the minimum weight of an atomic power generator is 100 tons.

The Atomic Energy Commission has initiated a development program which has for its object the study and use of atomic energy generators, or reactors, as they are called. Several types of these are under construction, or will be attempted in the near future, (a) a reactor designed to produce neutrons at a high rate which can be used in the study of materials, so that future reactors and equipment will have optimum characteristics as far as these are concerned, (b) a reactor suitable as a power source for naval vessels, (c) a reactor whose function is to "breed" more fissionable material than is at first present in the pile (operation "Bootstrap"), as well as to yield energy, (d) a reactor to produce

power. These projects are largely being carried out in government plants, through government subsidy to private industry.

Self Study Questions

1. Describe briefly the evidence which led to the first study of natural radioactivity.
2. Give in chronological order three methods used to detect the presence of radioactive substances.
3. Distinguish between alpha particles, beta particles, and gamma rays. How do they differ in behaviour in a magnetic field?
4. Describe two ways in which naturally radioactive substances in the earth's crust break up. Give the effects of these changes upon atomic number and atomic weight. Explain.
5. What is the average life expectancy of a uranium atom?
6. If the average life of a radium atom is only 2500 years, explain why all radium has not long ago disintegrated.
7. Explain how the age of uranium-bearing rocks can be established.
8. What is meant by the term "artificial radioactivity"? Illustrate.
9. Describe the first experiment carried out in which transmutation of elements was proven to have taken place.
10. Give other examples of the conversion of one element into another.
11. How are atomic numbers and weights shown in writing equations which show nuclear changes?
12. What is the element, its atomic number and weight, in the following cases?
 $_{4}\text{Si}^{28}$ $_{12}\text{Mg}^{24}$ $_{56}\text{Ba}^{137}$ $_{29}\text{Cu}^{65}$ $_{10}\text{Ne}^{22}$ $_{47}\text{Ag}^{109}$
13. Show in a similar manner atomic numbers, weights, and symbols for the most common isotopes of zinc, molybdenum, tin, mercury, and radium (see table of elements, front of book).
14. How many neutrons are in the nucleus of the selenium isotope $_{34}\text{Se}^{76}$?
15. What subatomic particles are used for bombarding nuclei? How can each be generated?
16. Describe briefly the operation of the cyclotron. What particles are accelerated in this device?

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17. Give three phenomena of great interest and importance which occur when ${}_{92}\text{U}^{235}$ or ${}_{94}\text{Pu}^{239}$ nuclei are hit with slow neutrons.

18. How do we account for the great amount of energy released during the fission of uranium or plutonium nuclei?

19. What is meant by a chain reaction? Is this sort of reaction necessarily limited to nuclear reactions?

20. What nuclear changes take place in a uranium pile?

21. Why is graphite included as part of this pile?

22. Name several other substances whose nuclei undergo fission when bombarded with high energy deuterons.

23. What is a deuteron? What is a positron? How are these subatomic particles obtained?

24. In the Einstein equation $E = mc^2$, where m is in grams and c is in centimeters, and E is ergs of energy obtained, calculate the number of ergs of energy formed when one gram of matter disappears.

PART FIVE

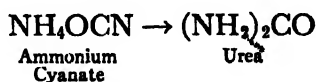
**Coal and Petroleum;
The Hydrocarbons**

XIII

Coal; Petroleum

Organic Chemistry. In the early days of chemistry, material substances were regarded as being of two kinds, those associated with inanimate nature, such as quartz and calcium sulfate, and those made within living cells, like sugar or beef tallow. The former were called "inorganic" and the latter "organic," and the branches of chemistry which dealt with these substances received the same names. Organic substances in those days were hence associated with life, and some mysterious vital force was thought to be necessary for their formation.

But during the first part of the last century the meaning of the term "organic" began to change as far as chemists were concerned. They began to find that some substances which had been regarded as typically organic could be prepared in the laboratory by chemical changes which required no living cells. Oxalic acid was probably the first chemical to be so prepared, by Wöhler (German) in 1824, and in 1828 the same scientist found that urea, the chief end product of nitrogen metabolism in the human body (page 437), could be made from the inorganic compound ammonium cyanate, in a rearrangement which required no loss or gain of material.



With the discovery of this last chemical change in particular the conviction began to grow in the minds of scientists that organic substances did not necessarily need living plants or ani-

mals for their formation, and this basis for calling substances organic or inorganic began to fall into disrepute. A difference in

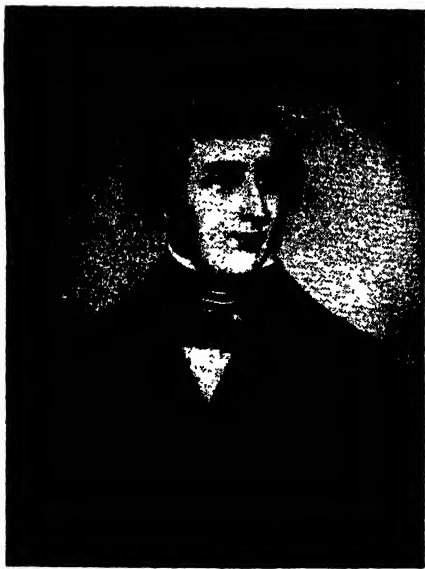


FIGURE 13.1. Friedrich Wöhler (1800–1882). This German chemist prepared urea from ammonium cyanate, thus helping to cause an important change in the thinking of scientists in regard to organic chemistry.

composition still remained between the two classes, however, because the organic substances were all compounds of carbon, whereas only a relatively few inorganic compounds contained this element. The newer distinction between organic and inorganic substances, based upon composition, has remained in use up to the present time, and organic chemistry today means the chemistry of the compounds of carbon.

The number of carbon compounds made in the laboratory now greatly exceeds the number which have been identified in living matter, and indeed, vastly exceeds all other compounds. The total number of known carbon compounds is now so great that no one has counted them, but it is thought to be somewhere in the vicinity of 500,000. This is about nine or ten times as great as the total of all other known compounds combined. Many organic substances are of great importance in our lives, and various branches of organic chemistry will occupy our attention for most of the remainder of the book.

The two most important fundamental sources of the many organic compounds made by the chemist are petroleum and coal. Both are also of great value as sources of power. These two natural resources will therefore be discussed briefly as a preliminary step before the study of organic chemistry.

COAL

Coal, chiefly carbon, is found in many places in the earth's crust, usually in seams of varying thickness. It is generally considered to be a mineral, although it does not have the definite chemical structure or the crystalline nature ordinarily required for mineral status. It is the product formed when plant matter is buried for long periods of time. Most of our coal now being mined was formed from plant life¹ buried several hundred million years ago. The process by which cellulosic material is converted to coal is not thoroughly understood, but there is probably some anaerobic bacterial action during the early stages of the burial, and later the effect of pressure and in some cases heat. The chemical changes which occur during this time are chiefly a loss of oxygen and a corresponding increase in the percentage of carbon. The process goes under the general heading of *carbonization*. Thus, the cellulose which largely makes up plant cells contains about 44 per cent carbon and nearly 50 per cent oxygen, while anthracite coal contains 80 per cent or more carbon and five per cent or less of oxygen. There is also a loss in hydrogen content as plant matter changes into coal.



FIGURE 13.2. Coal Seam. Courtesy Pittsburgh Consolidation Coal Company.

Types of Coal. Coal is divided into classes depending upon how far the process of carbonization has progressed. Table 13.1 shows the chief classes, together with analytical data. There are

¹ Largely reeds, mosses, ferns, and grasses that existed in swampy areas during the Carboniferous Period.



FIGURE 13.3. Different Types of Coal in Transportation. Courtesy Norfolk and Western Railway.

wide differences in composition, even for each class, hence the percentages shown are merely average values.

TABLE 13.1 Average Composition of Cellulose and Plant Matter in Different Stages of Carbonization

<i>Product</i>	<i>Percentage carbon</i>	<i>Percentage hydrogen</i>	<i>Percentage oxygen</i>
CELLULOSE	44	6	50
PEAT	51	6	34
LIGNITE	52	5	25
BITUMINOUS COAL	75	4	5
ANTHRACITE COAL	85	2	4

Small quantities of other substances are also present, including compounds of sulfur, nitrogen, phosphorus, silicon, and other elements.

Occurrence. Conditions for coal formation have been favorable in many places and at many times in the geological past, and numerous coal fields are known. There are six important regions in the United States, shown in Table 13.2.

TABLE 13.2 Important Coal Regions

<i>Region</i>	<i>Approximate total area, square miles</i>	<i>States containing largest fields</i>
EASTERN	70,000	West Virginia, Pennsylvania, Ohio, Kentucky
INTERIOR	130,000	Illinois, Missouri, Kansas, Iowa, Michigan, Oklahoma
GULF	2,000	Texas, Arkansas
NORTHERN	90,000	Montana, North Dakota, Wyoming
ROCKY MOUNTAIN	35,000	New Mexico, Wyoming, Colorado, Utah
PACIFIC COAST	2,000	Washington, Oregon, California

Coal is mined in 32 of the 48 states. This natural resource is man's principal source of energy, excluding the sun, of course. It is compared in this respect with petroleum, natural gas, and water power in Figure 13.4.

Destructive Distillation of Coal. A highly important industrial process is that of heating coal with an insufficient amount of air and collecting and utilizing the products. If coal were merely carbon there would be only oxides of a small portion of the carbon given off in this heating process. But the hydrogen and oxygen shown in Table 13.1, together with smaller amounts of other elements, are present in coal as complex organic compounds, and when coal is heated these break up to simpler, volatile products. Let us consider the most important of these.

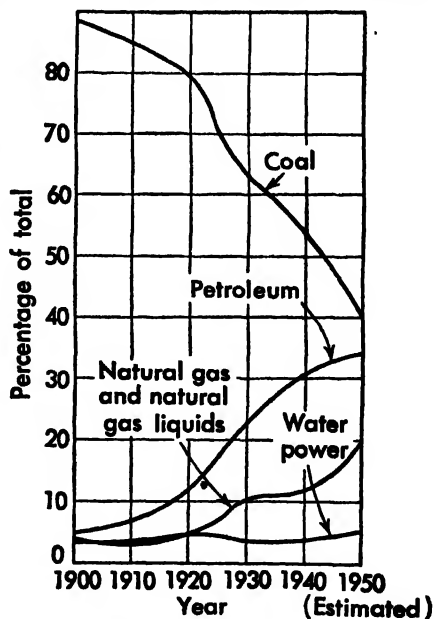


FIGURE 13.4. Production of Mineral Fuels and Power in the United States (Federal Power Commission).

Coal gas is one of the chief products given off when coal, usually bituminous, is destructively distilled. This is mainly hydrogen and methane (CH_4). Coal gas is used in many city homes for cooking and heating, although natural gas is preferred, in regions where it is available, because of its cheapness. A ton of bituminous coal produces about 10,000 or more cubic feet of coal gas. The product used in the home has been cleaned to remove substances such as hydrogen sulfide, ammonia, and benzene.

Coal tar is a thick black liquid distilled from coal. Its boiling range is much higher than coal gas, and after vaporizing from the heated coal it condenses a short distance from the still. Coal tar is the source of a number of organic chemicals, some of which will be described in the next chapter. About 100 pounds of coal tar are recovered from each ton of coal distilled.

Other chemical substances are condensed from the volatile products of coal distillation. These are taken out along with and after the removal of tar. They include ammonia, which is converted to ammonium sulfate (used for fertilizer), naphthalene (moth balls), and the substances benzene, toluene, and xylene, all important organic liquids.

Coke is left in the retort after the destructive distillation is complete. It is an impure form of carbon which is much in demand as a fuel, and as a reducing agent, e.g., in obtaining iron from iron ore. About 1400 pounds of coke remain after the volatile products have been driven off from a ton of coal.

PETROLEUM

Formation and Occurrence. All readers know that large reservoirs of naturally occurring oil are found at various locations and depths in the earth's crust. This material, petroleum, is believed to have been formed by the effect of pressure, and perhaps heat, upon buried organic matter from living things of long ago. Pockets of natural gas are associated with the oil in some locations, and are also found in the absence of paying quantities of oil.

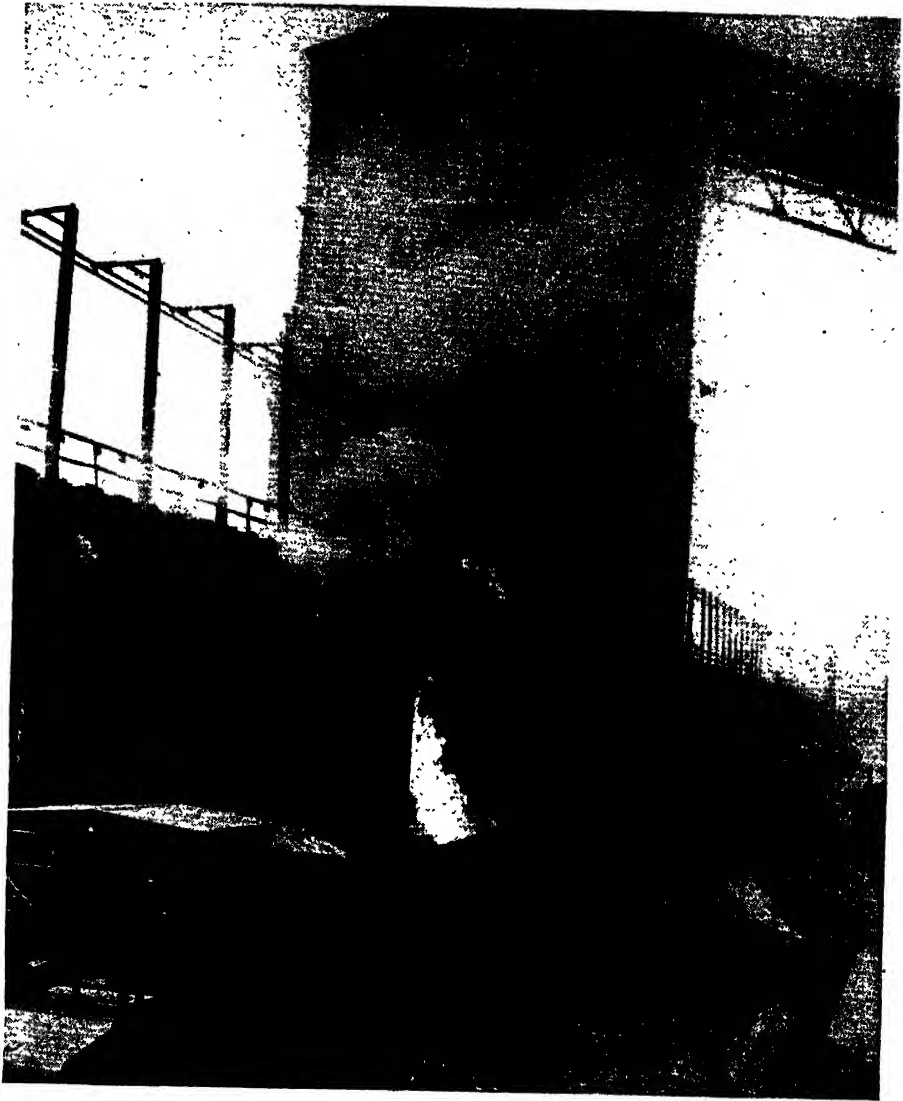


FIGURE 13.5. Coke Ovens at Clairton, Pa. Coal, heated with only a small amount of air in these narrow ovens, gives off important volatile products, including coal gas and coal tar, which are recovered. The hot coke residue is then pushed out laterally, as shown in this photograph. The hot coke goes to the quenching tower and then to the bin on the right. This by-product coke plant is the largest in the world, and consumes 30,000 tons of coal daily. Courtesy Bituminous Coal Institute.

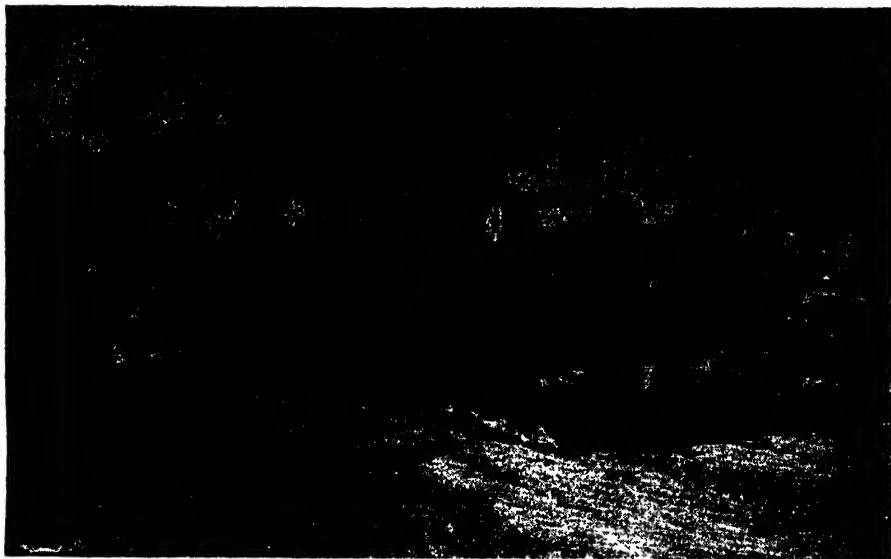


FIGURE 13.6. The Coal Industry Mechanizes. This continuous coal-mining machine can produce a four-ton flow of coal each minute in a coal seam only four feet high. Courtesy Bituminous Coal Institute.

It is recognized that certain geological conditions are required in order for petroleum to concentrate. These include (1) a source rock containing organic material from which oil can be formed; (2) a porous reservoir rock, such as sandstone, in which oil can accumulate; (3) a favorable structure, such as an anticline, shown in Figure 13.7, and (4) an impervious rock layer as part of the anticline, to cap the reservoir rock. This completes the trap. Frequently oil is forced into such a trap by underlying, denser water which exerts pressure upon it from below. This pressure was the cause of the gushers which formerly occurred, before they were outmoded by modern conservation methods.

While the occurrence of petroleum in the earth has been known for a long time, its use in large quantities to yield commercially important products began with the development of the Drake well, near Titusville, Pa. This well, drilled with considerable difficulty to a depth of 69.5 feet (10,000 foot wells are now not uncommon), began yielding oil on August 29, 1859. This started a boom which had a much greater significance than

the California gold rush, and within a few years kerosene obtained from petroleum had largely replaced whale oil in the lamps of the world. Some time later, with the coming of the automobile, the emphasis shifted away from the kerosene fraction of petroleum to the gasoline and lubricating oil fractions, but the substance has remained to this day one

of the great natural resources, guarded and sought by all nations.

Since the drilling of the Drake well, which lies in what is now known as the Eastern oil fields, many other regions have become oil producers. Chief of these in this country are the Mid-

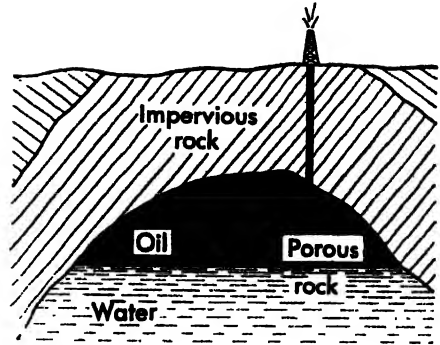


FIGURE 13.7. Conditions Necessary for Petroleum to Concentrate.

continent (Oklahoma, Kansas, Arkansas, Texas), the Californian, and the Gulf Coast regions. A major field also appears to be opening up at the present time in the vicinity of Edmonton, Alberta. In other parts of the world there are important fields in Mexico, Europe (Baku, Caspian area), South America (Colombia, Venezuela, Ecuador), Asia (Turkestan, Iraq, Iran, Burma, India, Sumatra, Java), Africa (Egypt).



FIGURE 13.8. Searching for Oil. The force of gravity is being determined here (Southern Louisiana), since this may give some indication of the presence of oil-bearing rock. Courtesy *The Sohian*, published by the Standard Oil Company of Ohio.

Methods of Finding Petroleum Deposits. Of great importance are the procedures used to locate oil, or to show the

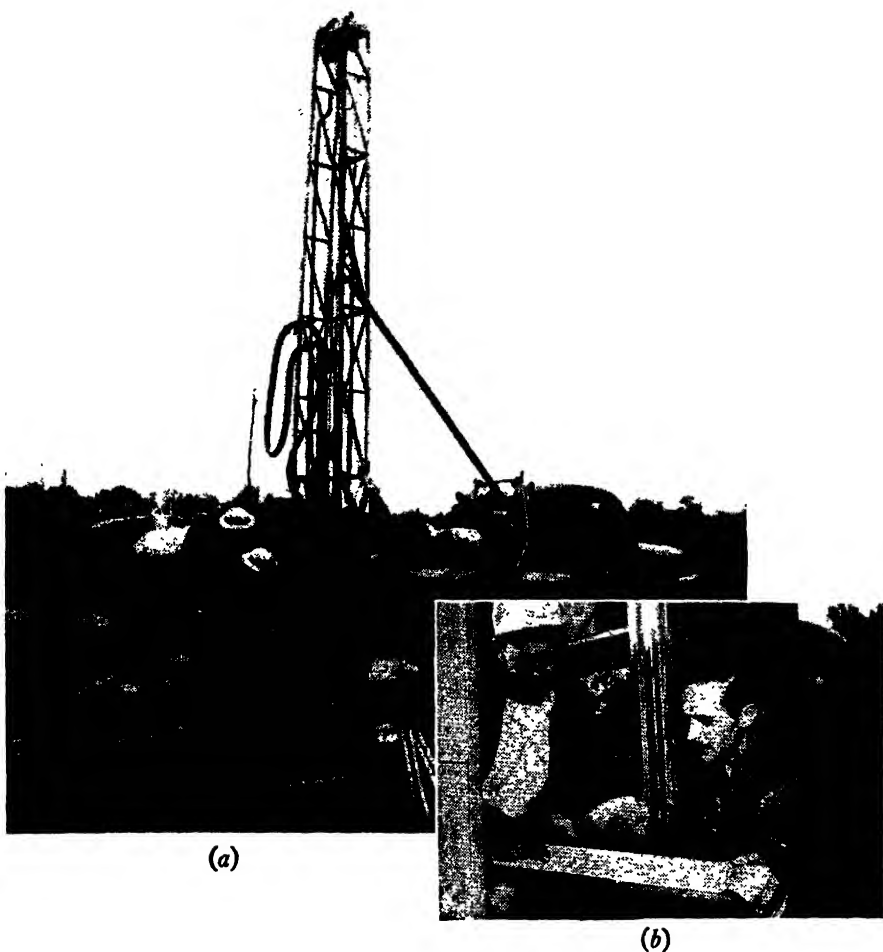


FIGURE 13.9 Searching for Oil. (a) A hole is being drilled, usually not over 100 feet deep, in which a charge will be exploded. (b) Seismograph recordings of the shock waves produced by the explosion. These may give some indication of oil concentrations. Courtesy *The Sohian*, published by the Standard Oil Company of Ohio.

likelihood of its presence. At first obvious signs were employed, such as oil springs or gasseeps. Geological methods were then used, as for example the predicting of an anticline which might be an oil trap from the slope of the surface rocks. These methods have now

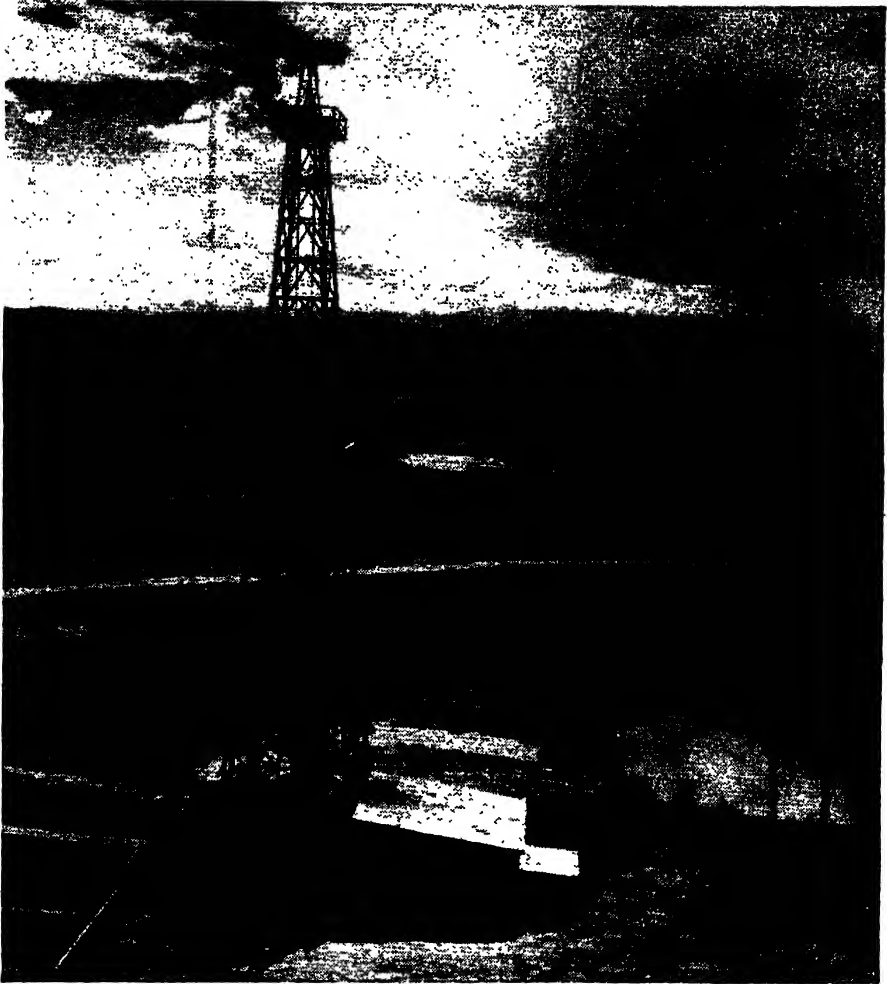


FIGURE 13.10. An Oil Well. Elk Basin, Wyoming. Courtesy Standard Oil Company of New Jersey.

been supplemented by various geophysical procedures, such as measuring the force of gravity, the electrical resistance, the magnetic permeability or the manner in which shock waves from an explosion reach a seismograph in a given region. Data from these measurements may give some indication of the presence of oil.

Fractional Distillation of Petroleum. Petroleum consists chiefly of a complex mixture of hydrocarbons (compounds con-

taining only hydrogen and carbon), which differ considerably in different oils. Some types of petroleum are rich in molecules



FIGURE 13.11. Oil Well Drilling. The bit is being changed, which takes about ten minutes. But five hours is required, on the average, to pull up the pipe and put it together again. Courtesy *The Sohian*, published by the Standard Oil Company of Ohio.

having an open structure, while others contain large amounts of *cyclic* hydrocarbons, in which a ring of carbon atoms is present. These various types will be discussed in the next chapter.

A complete separation of petroleum into its different molecular species is an almost impossible task, but a separation into groups of hydrocarbons with different ranges of properties is brought about by *fractional distillation*. In this process a mixture of mutually soluble substances such as are present in petroleum is heated to boiling and the resulting vapor is led off a convenient distance and condensed, by cooling, to a liquid known as the *distillate*.

Under ideal conditions no chemical changes take place during the distillation. The various molecules merely vaporize and condense again. The vapor which forms is richer in the more volatile members of the mixture being distilled than the liquid from which it came. The first portions of the distillate therefore contain a greater percentage of the lower-boiling components than the original mixture.

As the distillation progresses the remaining undistilled liquid becomes poorer in volatile components and its boiling point rises. The composition of the vapor changes accordingly, as does that of the distillate. A fractional distillation, then, is characterized as it goes on by a rising boiling point and a shift in composition of the distillate from the more volatile to the less vola-

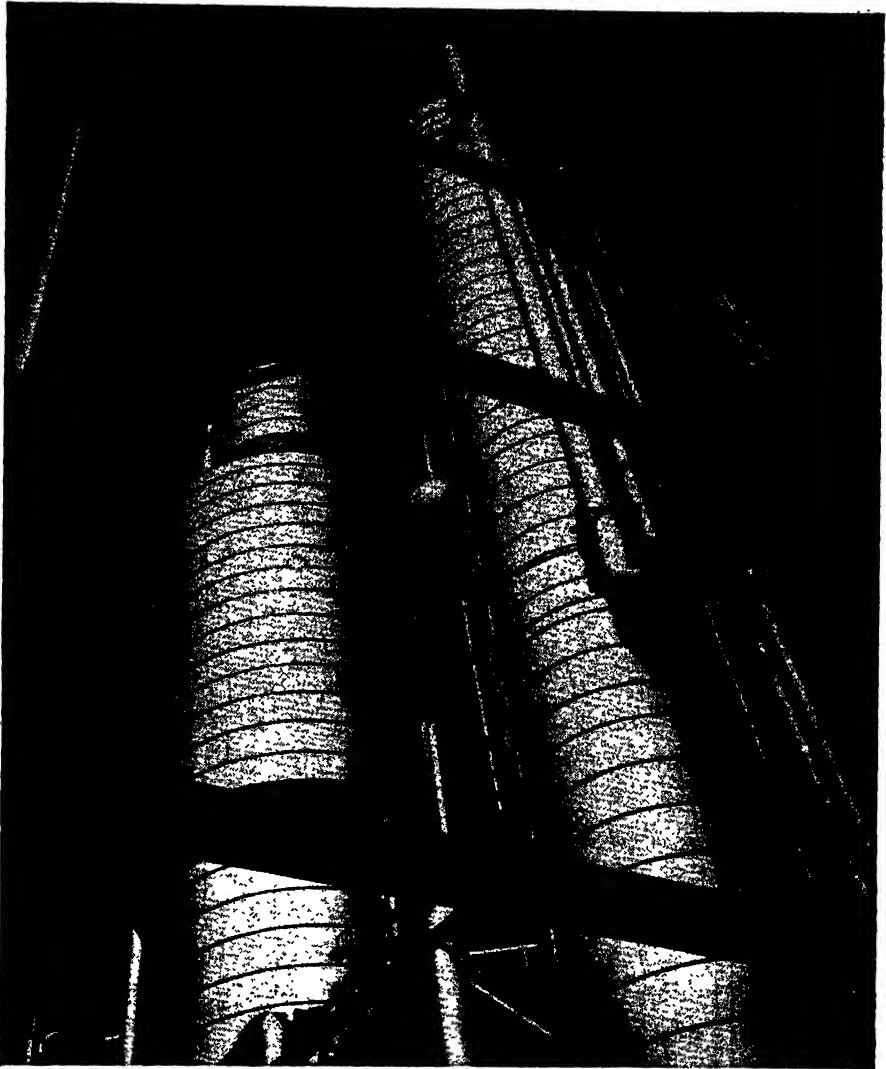


FIGURE 13.12. Fractional Distillation of Petroleum. These are called fractionating towers. Courtesy Socony-Vacuum Oil Company, Inc.

tile components of the mixture. By changing distillate receivers from time to time, or carrying out an equivalent process in a large-scale industrial distillation, a separation of the original mixture into fractions of varying volatility and composition can be effected.

In some distillations such a high temperature may be reached

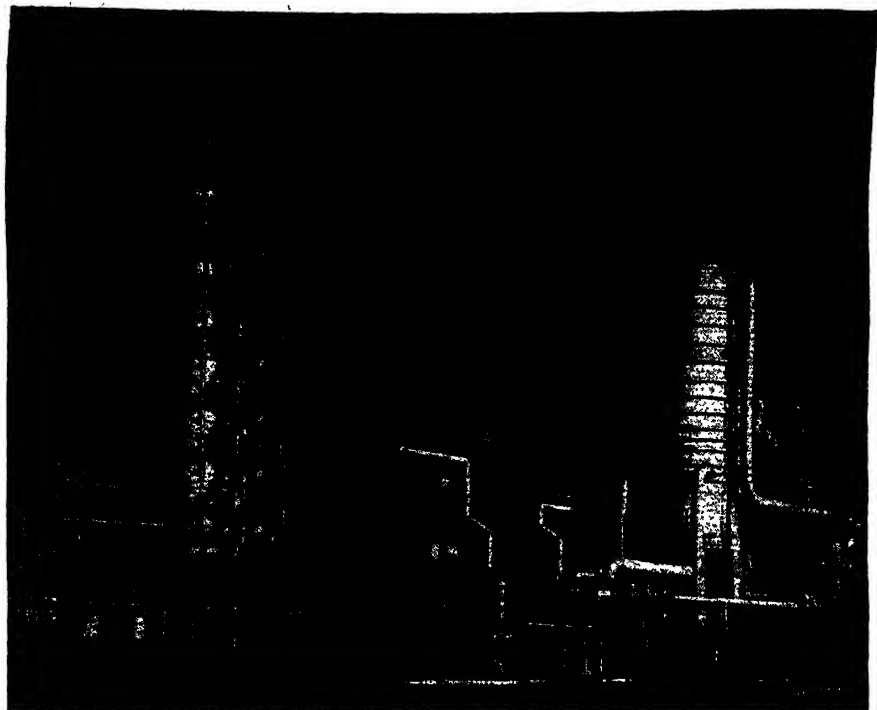


FIGURE 13.13. Pipe Stills. Atmospheric pipe still on the left, vacuum pipe still on the right. Courtesy Standard Oil Company of New Jersey.

before the completion of the process that chemical decomposition takes place rather than distillation. This would happen, for instance, if one were to attempt to distill sugar. To avoid such decomposition, or at least to put it off until a later stage, mixtures are distilled under reduced pressure, giving a lower temperature of boiling. Water, for example, boils at 100°C . at atmospheric pressure, but at 46.1°C . under a pressure of a tenth of an atmosphere (76 mm.).

The fractional distillation of petroleum is an important industrial process. The crude oil is treated in various ways, but one common procedure is first to distill off the most volatile components in a crude still (gasoline, kerosene, gas oil) and then to transfer the residue to a vacuum pipe still, for the reason described in the last paragraph. This gives additional gas oil and higher boiling fractions from which lubricants are made. With

certain types of crude oil a residue, known as asphalt, remains in the still. The fractional distillation of crude oil is only the beginning in the process of petroleum refining, and each of the fractions is treated in one or more ways to give desirable products.

IMPORTANT PETROLEUM PRODUCTS

Gasoline. Gasoline is a volatile mixture of hydrocarbons which was originally obtained only by the fractional distillation of petroleum. The product, known as "straight-run" gasoline, consists of hydrocarbons of low molecular weight. Gasoline is now so much in demand that our supply of petroleum is not nearly large enough to yield a sufficient quantity of this product by distillation alone. Straight-run gasolines, furthermore, often explode prematurely in the cylinders of automobile engines, producing knock, and they therefore require blending and the addition of antiknock agents.

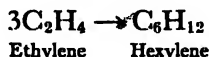
One additional source of gasoline is natural gas. The latter is sometimes found to be saturated with gasoline vapor, and by passing the mixture through suitable absorbents the gasoline fraction can be taken out and recovered, yielding the product *natural gasoline*.² Some 70 million barrels of this are produced yearly. It is so volatile that it is usually blended with less volatile hydrocarbons to produce a satisfactory gasoline.

But the total of straight run and natural gasoline is still far short of requirements. Fortunately other methods, chemical rather than physical in nature, have been devised for making the product. These are of two general types, (a) formation of gasoline molecules by the breaking up of larger hydrocarbon molecules with heat, pressure, and catalytic action, (b) synthesis of gasoline molecules from smaller molecules. This includes what may some day be our chief process, preparation of gasoline from coal and water.

² Natural gasoline, of controlled quality, has replaced the earlier indiscriminate product "Casinghead" or "Drip" gasoline, which used to accumulate in the liquid traps of the gas lines leading from the well heads.

The making of gasoline by decomposition of larger molecules to smaller ones comes under the general heading of "cracking." At first this was accomplished by using high temperatures, (thermal cracking) up to 700°C., accompanied by high pressures (to keep the size of equipment within reason, and later to insure good heat transfer). This treatment caused such violent thermal agitation of the molecules that they broke into smaller fragments; many of which were in the gasoline range. Later, techniques were developed in which catalysts were used ("Cat" cracking). This permitted lower temperatures and, particularly, lower pressures to be employed. The fraction of petroleum which can be converted into gasoline has been increased by the use of cracking from about one fifth to over two fifths.

The building up of gasoline molecules from smaller molecules (synthesis) is a newer development. It is accomplished by two general methods. One is *polymerization*, which is the joining together of two or more like molecules (monomers) to form a larger molecule (polymer). Thus, ethylene (page 337) can be polymerized to molecules in the gasoline range by the union of three or four of the monomers, i.e., ethylene molecules.



This is accomplished by the use of heat and catalysts. Another method is *alkylation*, used during the last war to produce aviation gasoline of high antiknock rating. Here, a reaction is brought about between isobutane (page 333) and various olefins (page 337). For example:



Our petroleum reserves are far from exhausted, but some day they will be, and oil men are looking forward to the time when other sources of gasoline must be used. One of these is tar sands, which are mixtures of sand and tarry material. These are plentiful in Canada, particularly around Athabaska, in Alberta. Another potentially large source of gasoline is oil shale. This is

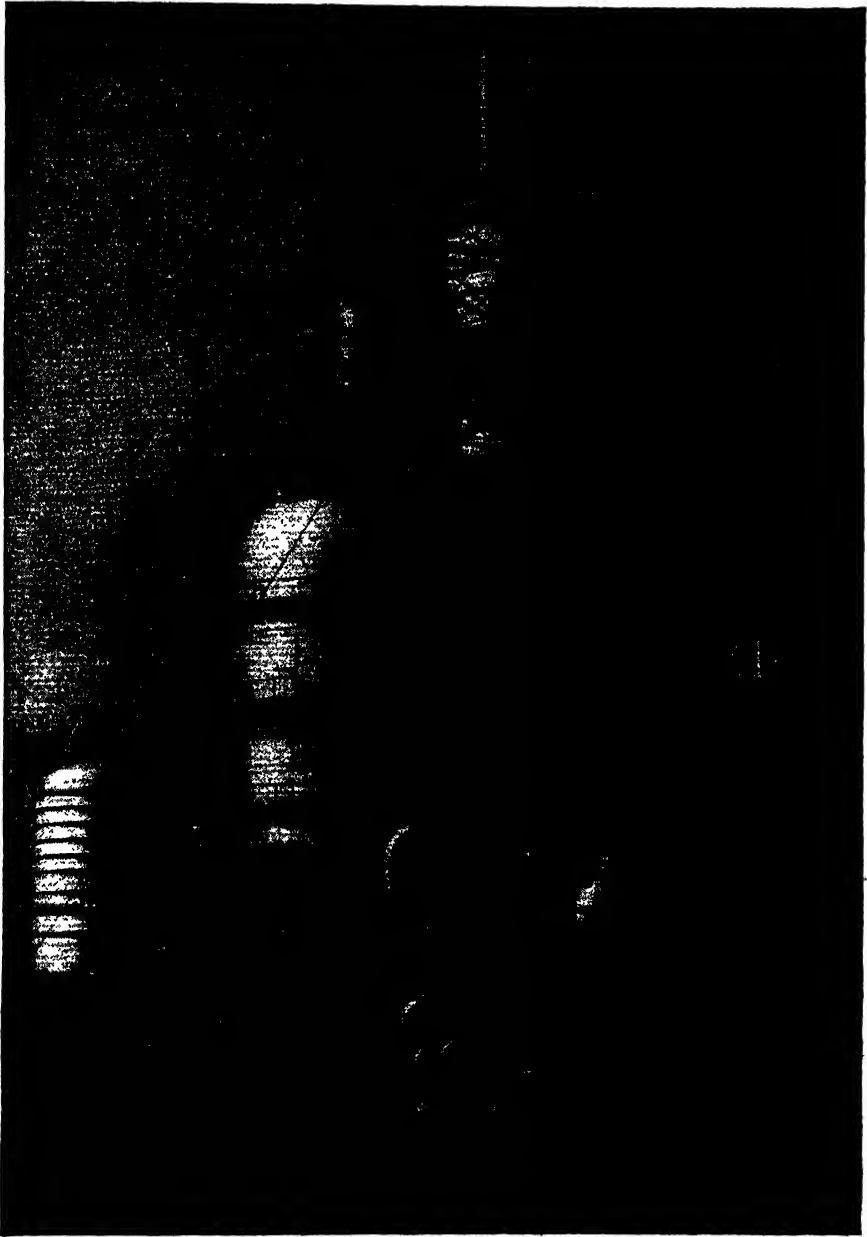


FIGURE 13.14. Gasoline Production. Catalytic cracking unit which employs a “fluid” catalyst, a fine, clay-like powder which circulates with the vapors and catalyzes breaking of large hydrocarbon molecules to smaller ones in the gasoline range. Courtesy *The Sohian*, published by the Standard Oil Company of Ohio.

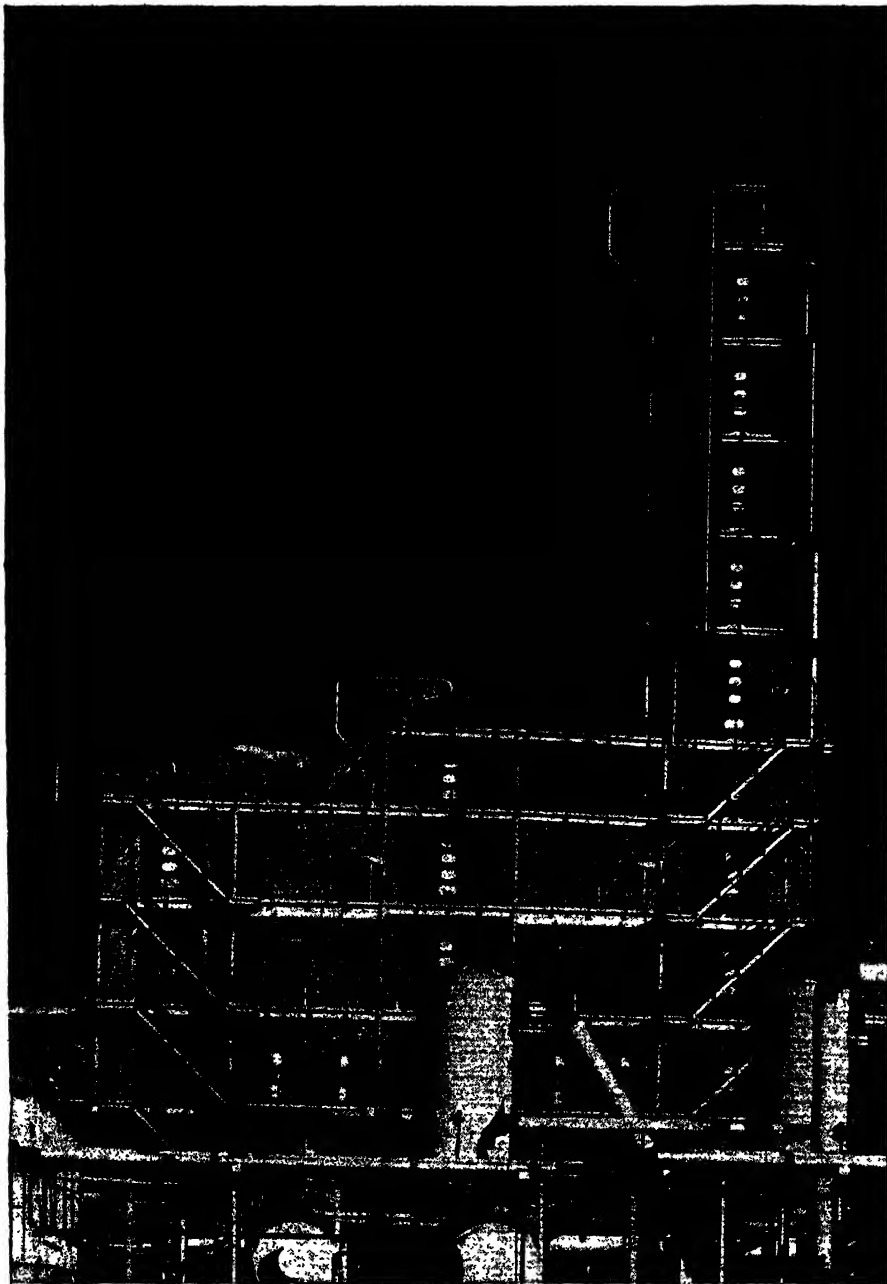
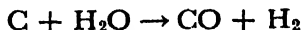


FIGURE 13.15. Gasoline Production. An alkylation plant. Courtesy Standard Oil Company of New Jersey.

a hard, slate-like rock which gives off a product resembling petroleum when it is heated. Oil shale varies considerably in its oil content, but the better grades average around 20 gallons of crude oil per ton of shale. Enormous deposits exist, chiefly in California and in the Colorado-Utah and Indiana-Illinois regions in this country.

However, the method of the future in gasoline manufacturing may well be a synthetic process developed in Germany and considerably improved in this country. This is the Fischer-Tropsch synthesis for preparing gasoline, Diesel fuel, alcohol and other compounds from coal, natural gas, or any combustible material containing carbon. If coal is the starting source of carbon this is converted to coke and allowed to react with steam in a process which yields *water gas*, a mixture of carbon monoxide and hydrogen.



In the Fischer-Tropsch process this mixture is now sent through batteries of synthesis reactors where in the presence of catalysts and high temperatures the two, simple, entering types of molecules are broken up and the elements recombine to form gasoline molecules and many others. The process was employed in Germany during the past war, and has been improved in this country by the use of "fluid" catalysts (solid substances in finely divided form which "flow" around the inside of the reactors without clogging them up). Natural gas makes a better starting material than coal, but any combustible carbon compound can be used, even such things as cornstalks or garbage.

One of the problems in gasoline manufacture is the prevention of "knocking" during the combustion of gasoline-air mixtures in engine cylinders. Knocking is apparently produced by a premature explosion of the part of the gasoline-air mixture which would otherwise be the last to burn (end gas). It appears to be caused by compression and by heat radiation from the part already burning. The tendency to knock is especially pronounced in gasolines which consist of the unbranched chain paraffins, such as *n*-heptane (page 331), and this becomes even worse in

high-compression engines, where the gasoline vapor-air concentrations are increased. Knocking is diminished or prevented by the addition of small quantities of lead tetraethyl ($\text{Pb}(\text{C}_2\text{H}_5)_4$), by the use of branched chain hydrocarbons (page 333) and by the addition of aromatic hydrocarbons (page 344). The first two additives are currently used in the formulation of automotive gasolines, while the second, and particularly the third, are used in the formulation of aviation gasoline.

Kerosene. Kerosene is the portion of the petroleum distillate which comes off after straight-run gasoline. It contains a large number of different hydrocarbons, open and closed chain (page 328), having from about ten to about eighteen carbon atoms per molecule. Kerosene was at one time the chief product in the distillation of petroleum, but it is now of much less importance than gasoline. It is used for illumination (kerosene lamps), for cooking (kerosene stoves) and for Diesel and jet engines. Kerosene has a considerable variation of properties depending upon the petroleum and the temperature range over which the fraction is collected. A good kerosene should have a fire point above room temperature, i.e., it should be possible to plunge a lighted match into a sample of kerosene at room temperature without igniting it.

Lubricating Oil. The residue left after distilling gasoline, kerosene, and gas oil from petroleum is treated in different ways in different refineries. In some plants this residue is called fuel oil, and it is sold without further processing. In other plants another distillation of the residue is made from a large structure known as a vacuum pipe still (Figure 13.13). The distillation temperature is lowered by using near vacuum conditions. This inhibits decomposition, and much of the residue from the earlier distillation can be successfully fractionated. Part of this distillate, after further treatment, is converted into lubricating oil of the type used in automobiles.

The treatment consists of several steps, some of which may be omitted with certain oils. The products are filtered through

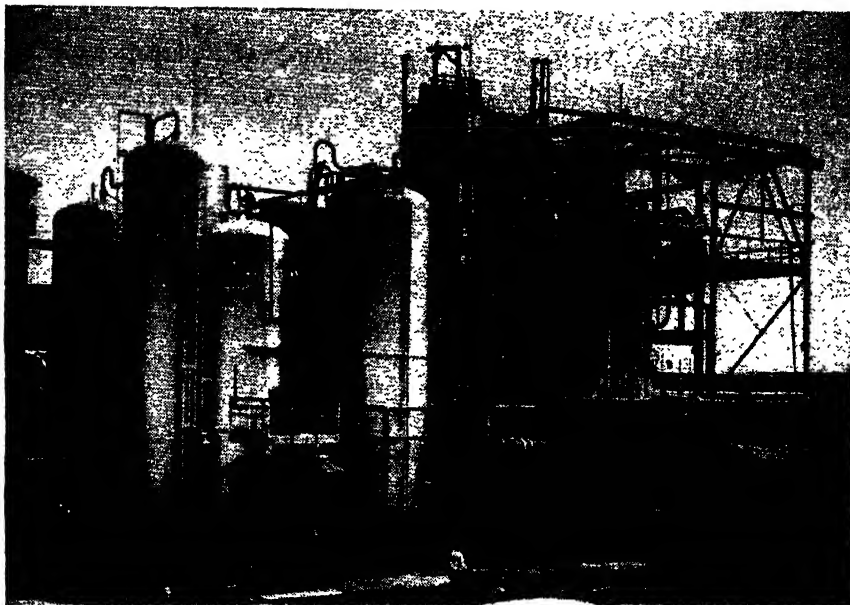


FIGURE 13.16. Lubricating Oil. The oil is cooled in this unit, causing wax to separate out. Courtesy *The Sohian*, published by Standard Oil Company of Ohio.

clay (or clay is added to the oil). Washing with sulfuric acid may be employed. The oil is usually cooled to cause wax to separate, and the latter is filtered off. The wax-free oil is a superior product since it continues to flow at lower temperatures than if the wax were present. The oil may be treated with solvents to remove undesirable portions (solvent extraction process). The product left after these treatments is a refined oil having about 20 or more carbon atoms to the molecule.

Petroleum hydrocarbons are not the only liquids used for lubrication. Organic compounds containing oxygen, sulfur, chlorine, or phosphorus in combined form, soaps and organic silicon compounds (silicones) are also employed.

Paraffin Wax. Paraffin wax is chiefly a mixture of unbranched hydrocarbons of the paraffin type (page 337) which is recovered as a by-product during the refining of lubricating oil. The molecular weights and boiling points of the molecules in the

wax are in the same range as those of the hydrocarbons in lubricating oils. The manner of recovery is to cool the oil, usually to the neighborhood of 0°F. , whereupon paraffin wax separates out and is removed by filtering through canvas. Besides its familiar use in the home to cover jam and jelly containers, paraffin is employed in the manufacture of candles, and for water-proofing paper and fabrics. The cotton which covers copper wire is sometimes impregnated with it, to improve insulation and water resistance. It is used in laundry work to produce a gloss.

Petrochemicals. Today, many chemical substances are made from petroleum besides the classical distillation products. These compounds, often having in them other elements besides carbon and hydrogen, are made by chemically altering substances obtained from petroleum. They are known as *petrochemicals*. Unsaturated (page 328) molecules containing carbon and hydrogen are the source of many of these. To name just a few of the substances in this category, ethylene is made into *ethyl alcohol* (page 351) and *ethylene oxide*, an intermediate used to form *glycol* (page 359) and the *Cellosolves* (solvents). Ethylene is also the starting material from which *polyethylene* (plastics) is made. Propylene is converted to *propylene glycol* and *glycerine* (page 359), each with many uses. Butylene is changed to *butadiene* (synthetic rubber, page 472). Seven-carbon molecules from petroleum can be made into *toluene* (page 343) used in gasoline blending, as a solvent, and to make other compounds employed in many fields, but chiefly in dyes and explosives. Petrochemicals are growing in number, and in quantity manufactured, at the present time.

Self Study Questions

1. What is the present meaning of the term "organic" chemistry? Has it always had its present meaning? Explain.
2. What is the origin of coal? What change in composition takes place during its formation?
3. Name the important classes of coal in the order of increasing carbonization.

4. What is meant by destructive distillation? Name several important products which result from the destructive distillation of coal.
5. Calculate the average percentage yield of coal tar, and of coke, from coal, based on data given in this chapter.
6. What factors do you believe account for the pronounced downward trend in the percentage of power and fuel from coal (Figure 13.4)?
7. What conditions must be fulfilled for a profitable concentration of petroleum to occur in the earth's crust?
8. Describe what is meant by fractional distillation. Name some important fractions obtained in the distillation of petroleum.
9. Can you name five products found in the home obtained from petroleum?
10. Coal and petroleum apparently both come from what was once living matter. Loss of oxygen accompanies the formation of both products. Can you suggest any reason why two such different minerals as coal and petroleum should be formed under these conditions?
11. From what sources do we obtain gasoline at the present time? What future sources of crude oil will remain in nature when our present petroleum reserves become exhausted?
12. Describe the Fischer-Tropsch synthesis. What materials can be used as carbon and hydrogen sources?
13. What causes knock when gasoline is ignited in an engine? How is it avoided?
14. Describe how paraffin is obtained. Give some of its uses.

XIV

The Hydrocarbons

Compounds which contain only carbon and hydrogen are known as *hydrocarbons*. These make up some of our most important industrial products, such as gasoline, lubricating oil, rubber, and some plastics. They vary greatly in molecular complexity, from methane, with but five atoms per molecule, to substances like natural rubber, whose molecules contain thousands of atoms each. The simpler hydrocarbons are obtained from coal, petroleum and natural gas, or are made from compounds occurring in these. For purposes of organization, hydrocarbons are usually divided into two broad, general classes, depending upon whether the molecule is in the form of a closed or open chain of carbon atoms. Petroleum and coal each yield both types, but most of the open-chain hydrocarbons come from the former and some very important closed-chain hydrocarbons from the latter. There occur, too, hydrocarbon molecules made up of both a ring and an open chain attached to each other.

OPEN-CHAIN HYDROCARBONS

Open-chain hydrocarbons are classified according to whether they are *saturated* (not more than two electrons shared between pairs of carbon atoms), or *unsaturated* (four or six electrons shared by a pair or more of carbon atoms). After this fundamental subdivision hydrocarbons are further classified according to whether the carbon chain is branched or unbranched. This classification is shown in Table 14.1.

TABLE 14.1 Classification of Open-Chain Hydrocarbons

Open-chain hydrocarbons	Saturated	Unbranched chain (as in <i>n</i> -pentane)*	$ \begin{array}{ccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ \text{H} & - \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \text{H} \\ & & & & & & & & & \\ & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \end{array} $
		Branched chain (as in isobutane)	$ \begin{array}{ccccccc} & & & & & \text{H} & \\ & & & & & & \\ & & & & & \text{C} & - \text{H} \\ & & & & & & \\ & & & & & \text{H} & \\ & & & & & / & \\ & & & & & \text{C} & - \text{H} \\ & & & & & & \\ & & & & & \text{H} & \\ & & & & & \backslash & \\ & & & & & \text{C} & - \text{H} \\ & & & & & & \\ & & & & & \text{H} & \end{array} $
	Unsaturated	Unbranched chain (as in ethylene)	$ \begin{array}{ccc} & \text{H} & \text{H} \\ & & \\ \text{C} & = & \text{C} \\ & & \\ & \text{H} & \text{H} \end{array} $
		Branched chain (as in isobutylene)	$ \begin{array}{ccccccc} & & & & & \text{H} & \\ & & & & & & \\ & & & & & \text{C} & - \text{H} \\ & & & & & & \\ & & & & & \text{H} & \\ & & & & & / & \\ & & & & & \text{C} & = \text{C} \\ & & & & & & \\ & & & & & \text{H} & \\ & & & & & \backslash & \\ & & & & & \text{C} & - \text{H} \\ & & & & & & \\ & & & & & \text{H} & \end{array} $

* The prefix *n*- means *normal*, or unbranched. The lines between atoms in the formulas mean pairs of shared electrons.

Let us consider some important examples of these types, starting with the unbranched, saturated hydrocarbons like *n*-pentane in the table above. The simplest hydrocarbon of this type is methane.

Methane. Methane, CH_4 , is the chief substance present in natural gas, and an important component also of coal gas. It is sometimes given the name of *marsh gas*, because it is formed in the underwater decay of vegetable matter in swampy places. It also occurs in coal mines; mixed with air it produces the dangerous, flammable *fire damp*. It is a colorless gas, which

liquefies with difficulty (boiling point $-161.7^{\circ}\text{C}.$, freezing point $-182.6^{\circ}\text{C}.$).

In methane the four hydrogen atoms are arranged symmetrically around the carbon atom. These can be thought of as occupying the four corners of a tetrahedron, with the carbon atom in the center (Figure 14.1). The molecule is held together by shared electrons; to show this structure we can write:

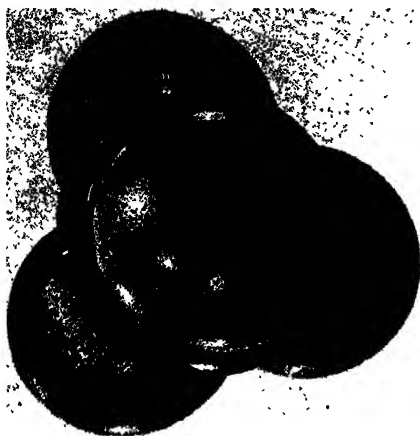
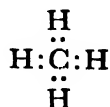


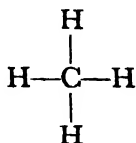
FIGURE 14.1. A Model of the Methane Molecule. Hydrogen atoms gray, carbon atom black. This model shows correct relative sizes and distances of atoms. Courtesy of Dr. J. A. Campbell.



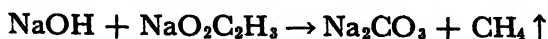
This is obviously not a good representation of the tetrahedron type methane molecule, and the reader should note that in general the structural formulas of molecules written on paper or the blackboard do not cor-

rectly show the actual three-dimensional structure of the molecules they represent.

The organic chemist often uses a single line between symbols in such formulas to show a pair of shared electrons. With this convention the structural formula of methane becomes:



Methane can be prepared in the laboratory by heating sodium acetate and sodium hydroxide.



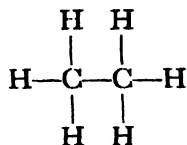
The substance is chemically rather inert, particularly at low temperatures. However, it burns in air or oxygen (page 72) and reacts with chlorine (page 337). Some important physical properties of methane and other unbranched *saturated* hydrocarbons are given in Table 14.2. By a saturated hydrocarbon is meant one containing the maximum amount of hydrogen, in which there are not more than two shared electrons between any two carbon atoms.

TABLE 14.2 Properties of the Unbranched Saturated Hydrocarbons

<i>Name</i>	<i>Formula</i>	<i>Liquid density</i>	<i>Melting point</i>	<i>Boiling point</i>	<i>Viscosity relative to water*</i>
METHANE	CH ₄	0.4240	-182.6°C.	-161.7°C.	
ETHANE	C ₂ H ₆	0.5462	-172.0	- 88.6	
PROPANE	C ₃ H ₈	0.5824	-187.1	- 42.2	
BUTANE	C ₄ H ₁₀	0.5788	-135.0	- 0.5	
PENTANE	C ₅ H ₁₂	0.6264	-129.7	36.1	0.24
HEXANE	C ₆ H ₁₄	0.6594	- 94.0	68.7	0.33
HEPTANE	C ₇ H ₁₆	0.6837	- 90.5	98.4	0.42
OCTANE	C ₈ H ₁₈	0.7028	- 56.8	125.6	0.54
NONANE	C ₉ H ₂₀	0.7179	- 53.7	150.7	0.64
DECANE	C ₁₀ H ₂₂	0.7298	- 29.7	174.0	0.79
DODECANE	C ₁₂ H ₂₆	0.7493	- 9.6	216.3	1.28
TETRADECANE	C ₁₄ H ₃₀	0.7636	5.5	251	2.13
HEXADECANE	C ₁₆ H ₃₄	0.7749	18.1	280	3.59
EICOSANE	C ₂₀ H ₄₂	0.7777	36.4	205 (15 mm.)	
HENTRIACONTANE	C ₃₁ H ₆₄	0.781	68.1	302 (15 mm.)	
HEXACONTANE	C ₆₀ H ₁₂₂	0.80	99		

* Thus the data in this column show hexane to be only one-third as viscous as water, while tetradecane is over twice as viscous.

Other Saturated, Unbranched Hydrocarbons. Consider next the substance *ethane*, C₂H₆. Its structural formula is shown below.



Here is shown the structure of an organic compound in which carbon is joined to carbon. Other elements exhibit this tendency to a limited degree, but carbon is by far the most outstanding

of the elements in this respect; as a result we have many more compounds of carbon than of all the other elements put together.



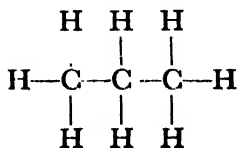
FIGURE 14.2. Liquefied Petroleum Gas. This mixture, chiefly propane and butane, forms a suitable heating and cooking gas when allowed to expand. It is used in suburban and ranch homes. Courtesy Standard Oil Company of Ohio.

Indeed, life as we know it could not exist on the earth if carbon did not behave in this way, because all living matter is built up from molecules in which carbon is joined to itself many times over.

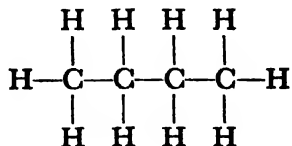
Ethane, C_2H_6 , differs from methane, CH_4 , by the increment CH_2 , and succeeding hydrocarbons in Table 14.2 are seen to differ from adjacent compounds by the same amount. A series of compounds which differ from each other by a constant amount, such as CH_2 , is known as an *homologous series*.

From the table just given methane is seen to have higher melting and boiling points and a greater density than methane.

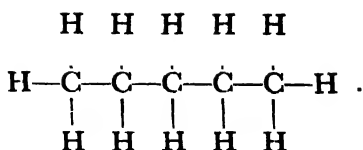
This is to be expected from the larger molecular weight and the greater percentage of carbon. This change in properties continues as we go to the more complicated hydrocarbons. The boiling point is seen to increase steadily, for example, as we pass from propane:



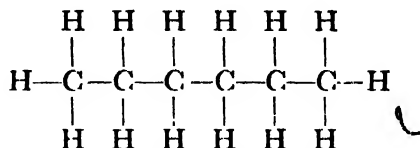
to butane:



to pentane:



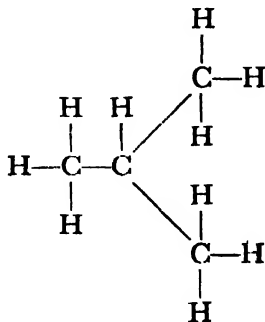
The latter substance is a liquid at room temperature, since it boils at 36.1°C. The hydrocarbons which follow this, from hexane



through to dodecane, are components of gasoline.

The viscosity is also seen to increase from pentane, about one fourth as viscous as water, to hexadecane, over 3.5 times as viscous. The viscosity, which determines how readily a liquid can be poured or stirred, becomes greater as the length of the molecule increases, because long molecules get in each other's way and hinder changes in the shape of a liquid. The reader is familiar with the high viscosity of some of the more complex hydrocarbons from experience with lubricating oil.

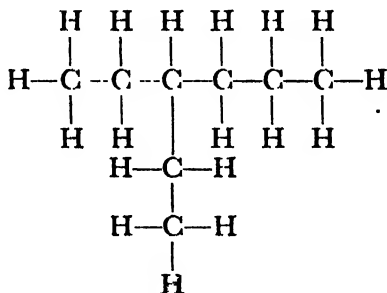
✓ **Saturated, Branched Chain Hydrocarbons.** Besides the unbranched hydrocarbons just mentioned, there is a large number with branched chains. The simplest of these is a molecule with four carbon atoms.



This substance is called *isobutane*. Hydrocarbons with more than four carbon atoms can have various kinds of branched chains.

When the branching is limited to two carbon atoms at the end of the molecule, as above, the prefix *iso* is attached to the name of the unbranched molecule with the same number of carbon atoms. Isobutane is therefore named from butane. Similarly we have isopentane, isohexane, etc. However, there is no isomethane, isoethane, or isopropane. To make the naming even clearer, the unbranched hydrocarbons are sometimes called *normal*. The abbreviation "*n*" is commonly used for this word, and is put in front of the name. Thus, the compounds given in Table 14.2 are all normal hydrocarbons, and could be called *n*-octane, *n*-decane, etc.

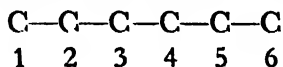
Many other branched hydrocarbons are known besides the iso compounds. Consider the following example with eight carbon atoms.



It is obviously different from *n*-octane or isooctane. For naming compounds like this chemists adopted the following rules at an international meeting in Geneva (1892).

(a) *Choose the longest unbranched chain of carbon atoms in the molecule. This will provide a basic hydrocarbon name for the substance.* In the above example the longest chain is of six carbon atoms, i.e., C—C—C—C—C—C. The basic hydrocarbon name is hence hexane.

(b) *Number the carbon atoms in this chain.* In the example we get

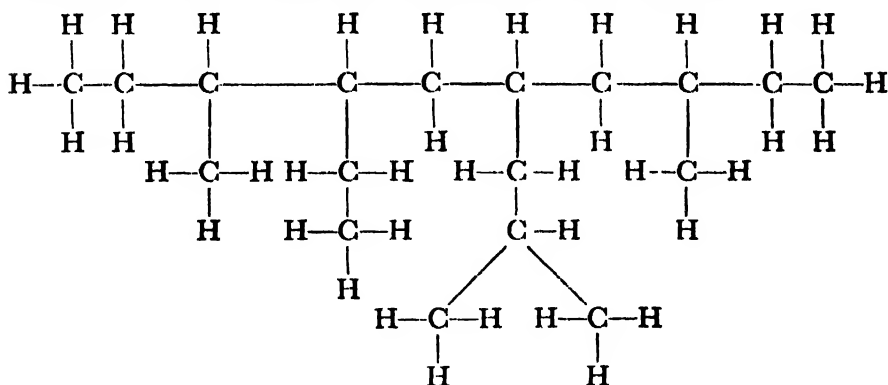


(c) *Name the groups attached to this longest chain and show their positions by using the number of the carbon atom to which each is attached. In naming, group names come first and the basic name goes last.* The substance in the example is therefore 3-ethylhexane.

The name *ethyl* for the C_2H_5 group needs explaining. Any hydrocarbon, *minus one hydrogen atom*, can be attached as a group to a molecule. The point of attachment is by the carbon valence which is free because of the missing hydrogen atom. This group is then named like the hydrocarbon from which it is derived, except that the ending *-yl* is substituted for the hydrocarbon ending *-ane*. Thus we get names such as the following.

roup name	Group formula
METHYL	$-CH_3$
ETHYL	$-C_2H_5$
PROPYL	$-C_3H_7$
BUTYL	$-C_4H_9$
PENTYL	$-C_5H_{11}$
HEXYL	$-C_6H_{13}$

Consider the following more complicated compound.



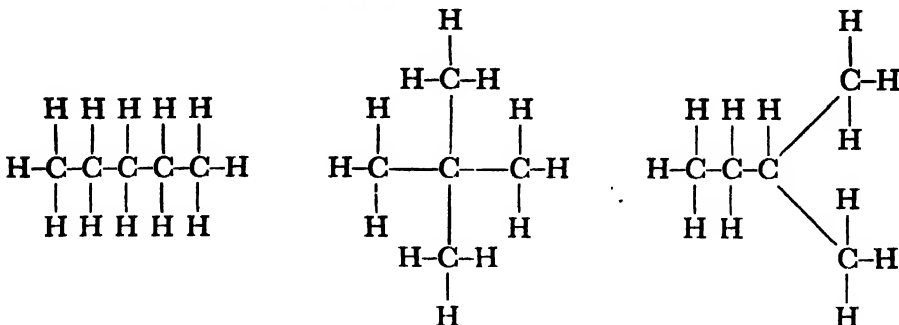
This is 3-methyl-4-ethyl-6-isobutyl-8-methyldecane.

Structural Isomers. Let us consider once more the two substances butane and isobutane. They each have the same condensed formula, C_4H_{10} , and therefore the same molecular weight and percentage composition. Substances in this category which have similar condensed formulas but different molecular structures are called *isomers*. There are several types of these; the ones now under consideration are known as *structural isomers*.

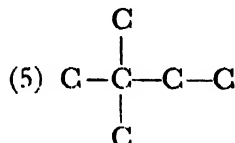
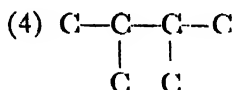
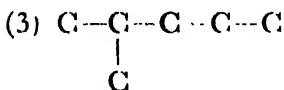
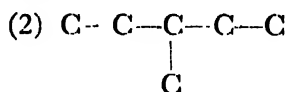
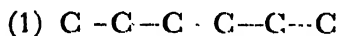
The number of possible structural isomers increases rapidly with the number of carbon atoms. Thus, there is only one

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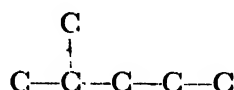
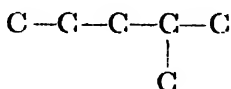
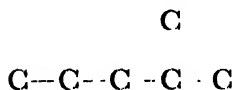
possible form of methane and ethane, and only one open chain form of propane. But there are two structural isomers of butane, the normal and iso compounds. There are three pentanes.



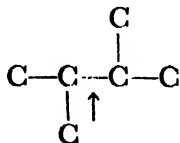
Note the possibilities with hexane. To make the carbon chains more obvious the hydrogen atoms will be left out (but there must be fourteen of the latter in each case).



There are therefore five structural isomers of hexane. Others may seem possible, but they are simply forms of these five written in different ways. Thus:

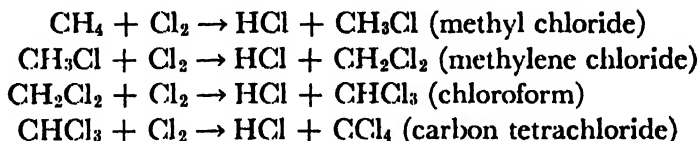


are merely molecule number (3) turned to a different position. Another variation which certainly appears different is:



However, it is the same as (4) above. This is so because *single* bonds between carbon atoms allow rotation of the two parts of the molecule they connect. Hence the form just given and (4) above are merely different shapes taken by the same molecule as the middle bond, shown by the arrow, permits rotation of the two halves.

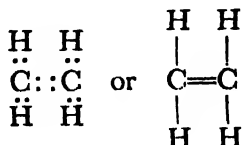
Chemical Properties of the Saturated, Open-Chain Hydrocarbons. Chemically the saturated, open-chain hydrocarbons are rather inert. They burn in air or oxygen at elevated temperatures to form carbon dioxide and water. They also react with the elements fluorine, chlorine, and bromine. Thus, chlorine reacts upon methane to give a series of products.



These chemical changes take place more rapidly in bright light, and in direct sunlight a mixture of methane and chlorine explodes. The reactions are hard to control, and the four named products are not made commercially in this way. Nearly all other chemical substances are without effect upon the open-chain, saturated hydrocarbons.

The hydrocarbons studied so far are sometimes known as the *paraffin* hydrocarbons, because the substance paraffin is made up of a mixture of the higher members. All paraffin hydrocarbons have the formula $\text{C}_n\text{H}_{2n+2}$.

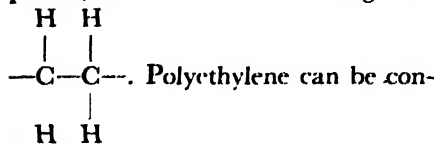
Olefins and Acetylenes. A large number of hydrocarbons are known in which there are four shared electrons between a pair of carbon atoms. The simplest is the substance *ethylene*.



This is a colorless gas which liquefies at $-102.4^{\circ}\text{C}.$ and solidifies at $-169.4^{\circ}\text{C}.$ When two carbon atoms share two pairs of electrons, they are said to be joined together with a *double bond*. The series of open-chain hydrocarbons having this characteristic

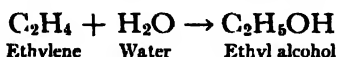


FIGURE 14.3. Polyethylene Plastic. Squeezable bottles and ice cube containers are made from this plastic, which has the building unit



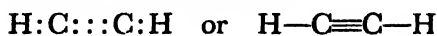
Polyethylene can be considered as an unusually high paraffin homologue.

Hydrocarbons containing double or triple bonds are chemically much more active than the saturated hydrocarbons. They tend to combine with other substances, and to polymerize. A number of important industrial processes are based upon this chemical activity. Ethylene, for example, is converted to ethyl alcohol (page 352) by taking on water in the presence of sulfuric acid. Leaving out the intermediate steps, we have:



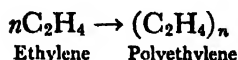
structure is known as the *olefins*. Such compounds contain less hydrogen than the corresponding paraffin hydrocarbons (compare C_2H_4 and C_2H_6 , for example), because fewer electrons are available for sharing between hydrogen and carbon. For this reason they are said to be *unsaturated*.

Compounds with an even higher degree of unsaturation are known, in which three pairs of electrons are shared by two carbon atoms, producing what is known as a *triple bond*. The substance acetylene is the first member of this series.

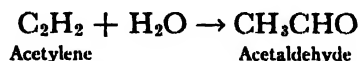


This colorless gas liquefies at $-83.4^{\circ}\text{C}.$ The series is called the acetylenes, after the first member.

Ethylene in the liquid state polymerizes to polyethylene, an important plastic (Figure 14.3).



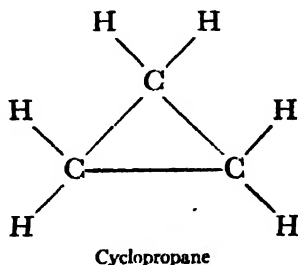
Acetylene combines with water in the presence of hot, dilute sulfuric acid and mercuric sulfate catalyst to yield acetaldehyde (page 356).



In other addition reactions or polymerizations, acetylene is converted to vinyl acetate (adhesives, plastics), Lewisite (war gas), vinylacetylene and isoprene (synthetic rubber), and other products. Large quantities of preformed acetylene are used for producing the blowtorch flame employed in the cutting and welding of metals.

CLOSED-CHAIN HYDROCARBONS

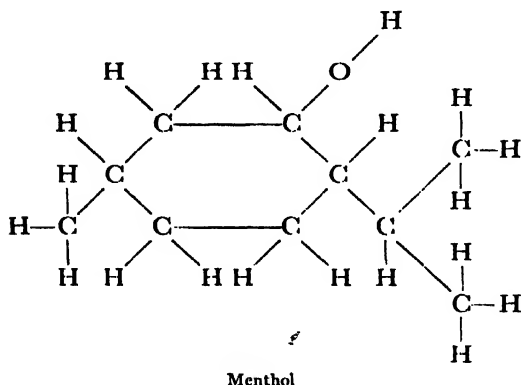
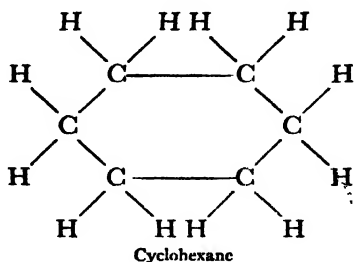
Cyclic Hydrocarbons from Petroleum and Natural Gas. Many hydrocarbons are known in which the carbon chain is closed, i.e., the carbon atoms are joined together to form a ring. The simplest of these is a three-carbon ring, found in the substance *cyclopropane*. This colorless gas, whose formula is shown below, is present in small quantities in some natural gas.



Cyclobutane, cyclopentane, and cyclohexane are also known. The latter substance has a number of derivatives which are found

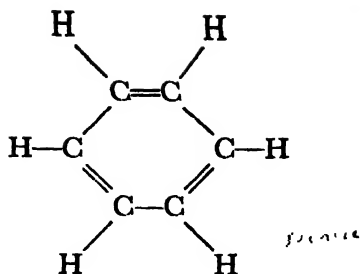
340 Coal and Petroleum; The Hydrocarbons

in the volatile, fragrant oils of growing plants. Menthol, present in oil of peppermint, is an example.

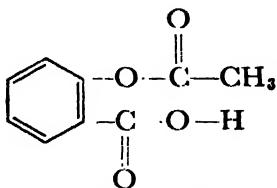


The saturated cyclic (closed-chain) hydrocarbons also occur in considerable quantities in some petroleum, usually with hydrocarbon side chains attached to them. They go under the general name of naphthenes in petroleum chemistry.

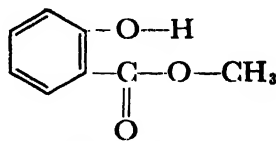
Cyclic Hydrocarbons from Coal. When coal is heated in the absence of air, the compounds of elements present other than carbon (chiefly hydrogen, oxygen, nitrogen, and sulfur), react with carbon, or with each other, to give volatile products which distill off, leaving behind a residue of coke. Among these volatile products are several important cyclic hydrocarbons. One of them is the substance *benzene*.



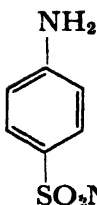
The formula for a benzene molecule is often drawn in the simplified manner shown at the right because it is used so frequently by organic chemists, the substance being of such importance that a whole branch of organic chemistry has been built up around it. This importance follows from its cheapness (large quantities are recovered from the destructive distillation of coal) and from its many uses, not only by itself, but in the making of other chemical derivatives. Consider, for example, a few of the well-known organic compounds whose basic structure is a benzene ring. These are shown below.



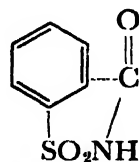
Acetylsalicylic acid
(Aspirin)



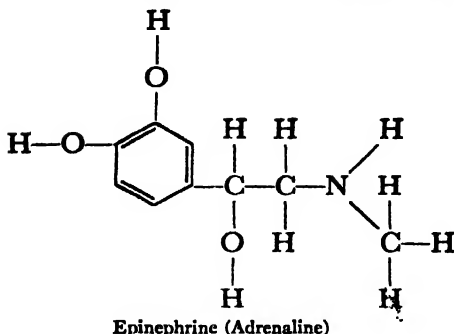
Methyl salicylate
(Oil of wintergreen)



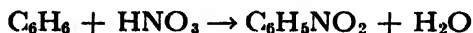
p-aminobenzenesulfonamide
(Sulfanilamide)



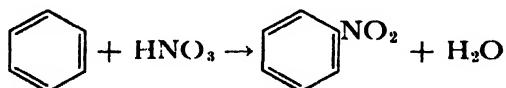
Benzoic sulfimide
(Saccharin)



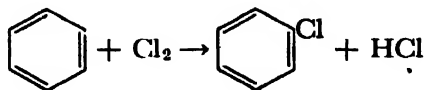
Benzene, or benzol as it is sometimes called, is a colorless liquid which freezes at 5.5°C . and boils at 80.1°C . It is sparingly soluble in water (7 parts per 10,000 at room temperature), but soluble in all proportions in alcohol and in ether. It undergoes a number of reactions. Thus, with nitric acid it forms *nitrobenzene* (oil of mirbane), $\text{C}_6\text{H}_5\text{NO}_2$.



Nitric acid breaks up differently in this type of reaction than when it dissociates into ions. The point where the molecule breaks is between oxygen and nitrogen, $\text{H}-\text{O} \times \text{NO}_2$. Sulfuric acid is usually included as a catalytic agent when this reaction is carried out. When the benzene ring, instead of the formula C_6H_6 , is used in the equation the reaction is written:



Benzene reacts with chlorine in the presence of a catalyst to form chlorobenzene.

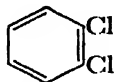


More chlorine can be put in the ring in the same way, forming different dichlorobenzenes. Three isomers of this substance can

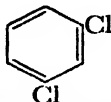


FIGURE 14.4. Turpentine. Resinous pine wood is about to be destructively distilled to yield D.D.Turpentine and other products. Turpentine is also obtained from pine gum from living pine trees (Gum Turpentine), and by solvent extraction of resinous wood (Wood Turpentine). Courtesy The Glidden Company.

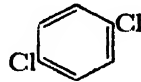
be made. Their formulas are shown below. The prefix *ortho* (*o*) is used when two substituents are on adjacent carbon atoms, *meta* (*m*) when one carbon atom is between, and *para* (*p*) when they are on opposite parts of the ring. Ortho- and metadichlorobenzene are liquids at room temperature but the para compound is a solid. It is widely used as moth crystals.



o-dichlorobenzene

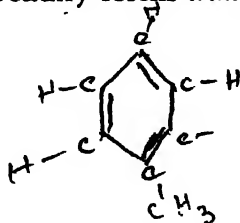


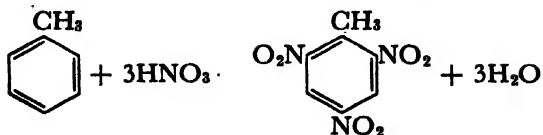
m-dichlorobenzene



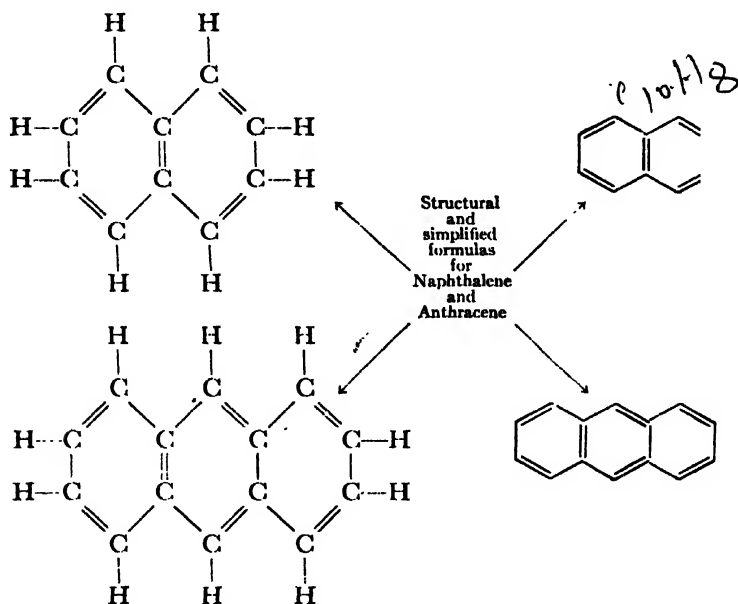
p-dichlorobenzene

Another important compound obtained during the destructive distillation of coal is *toluene*, or methyl benzene, $C_6H_5CH_3$. This is somewhat more reactive than benzene. For example, with nitric acid it readily forms *trinitrotoluene* or *TNT*, the well-known explosive.





Compounds are also recovered from coal tar which contain two or more benzene rings. In the substance *naphthalene*, familiar to the reader in the form of "moth balls," two such rings are joined together by the sharing of a side, and in the substance *anthracene* there are three. Both compounds are used in the manufacture of dyes.

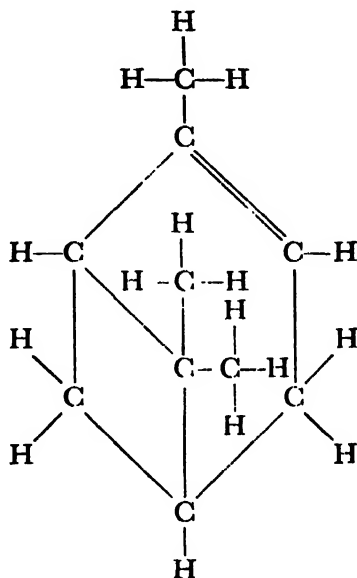


Benzene, toluene, and related substances are known as *aromatic* hydrocarbons, because of their odor.

HYDROCARBONS FROM PLANTS

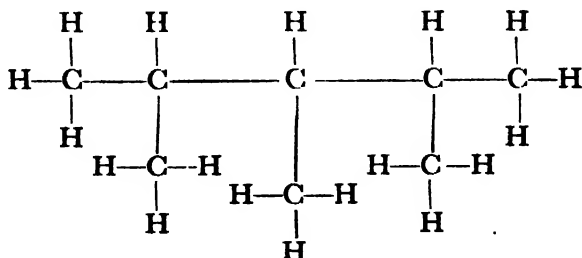
Volatile substances are found in the leaves and flowers of plants, and in the bark and wood of trees. These can be extracted, and have been since early times, to give products known as

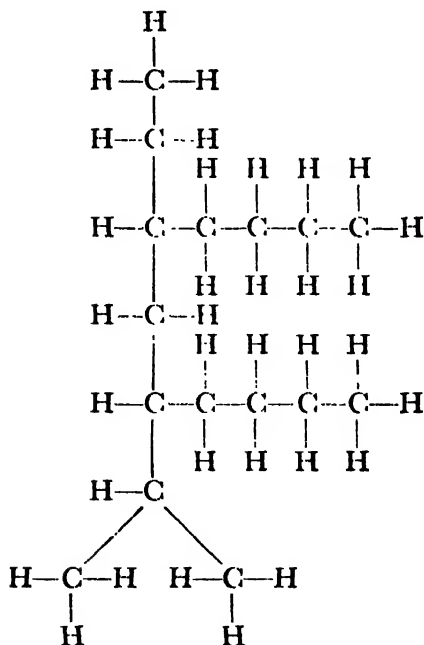
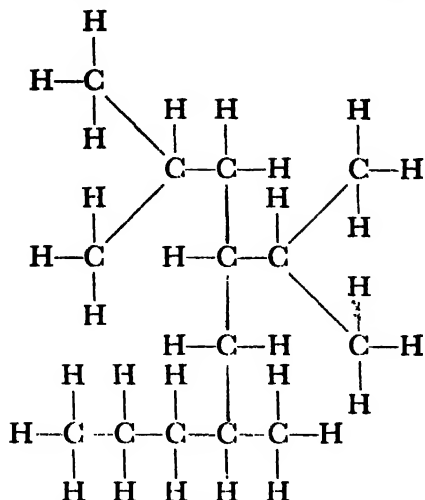
essential oils. Among the latter are many hydrocarbons which belong to a class of substances known as *terpenes*, isomeric compounds with the formula $C_{10}H_{16}$. An example is *pinene*, the chief component of turpentine (Figure 14.4).



Self Study Questions

1. Write structural formulas for ethane, pentane, octane. How do the *n*-hydrocarbons differ from the iso-hydrocarbons in each case?
2. Name the following hydrocarbons according to the Geneva system.

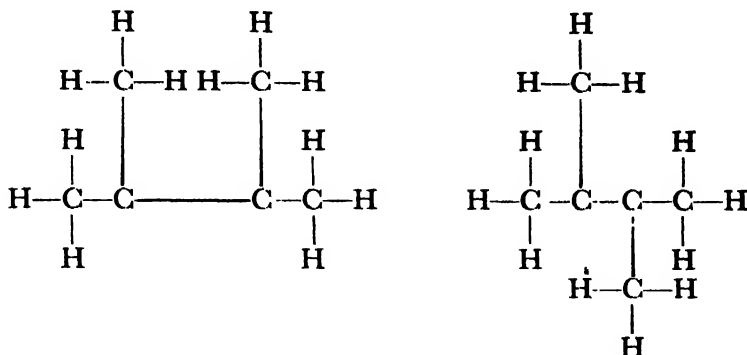




3. Write the structural formula for 3-methyl-4-isobutyl-4-ethyl-5-propyl-7-isopropyldodecane.

4. What are structural isomers? There are nine structural isomers of heptane. See if you can write them.

5. The two formulas written below are not structural isomers, but are merely different forms of the same molecule. Explain how this is possible.



6. Write equations showing the successive reactions of chlorine upon methane. Name the products formed.

7. What is an olefin? Write the structural formula for a butylene. Explain what is meant by a double bond in terms of shared electrons.

8. What is an acetylene? Write the formula of an acetylene containing four carbon atoms.

9. Write three equations showing characteristic reactions of olefins and acetylenes.

10. What is cyclopropane? Cyclohexane? Note that the general formula for the cycloparaffins, C_nH_{2n} , is the same as that for the olefins.

11. What are naphthenes? Where are they found?

12. Write structural formulas for benzene and toluene. What is the fundamental difference between benzene and cyclohexane? What simplification of the benzene ring is used in writing formulas and equations?

13. Write equations for the reaction of nitric acid upon (a) benzene, (b) toluene.

14. Assuming 85 per cent yield, what weight of nitrobenzene could be obtained by action of excess nitric acid upon 100 grams benzene?

Answer: 134 grams

15. How does chlorine react with benzene? What three isomeric dichlorobenzenes are known? How are they named to tell them apart?

16. Give examples of hydrocarbons from coal in which benzene rings are joined together by the sharing of a side.

17. Give an example of a hydrocarbon formed by a living plant. What is an essential oil?

PART SIX

The Food We Eat

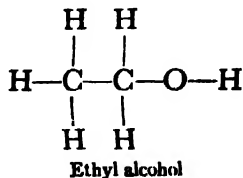
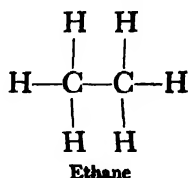
Alcohol;

Acetic Acid

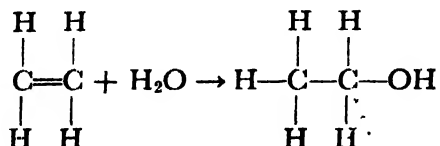
There may be some question as to the correctness of classifying alcohol and acetic acid as "foods." However, they are taken orally into the human system as part of alcoholic beverages and vinegars. They are included at this point chiefly because they are among the simplest organic compounds containing hydrogen and oxygen, and study of their chemistry prepares the reader for a better understanding of the more complex carbohydrates, fats, and proteins which follow.

ETHYL ALCOHOL

An alcohol is a substance whose molecule contains one or more of the groups $\begin{array}{c} | \\ -\text{C}-\text{O}-\text{H} \\ | \end{array}$, where the other three valences of the carbon atom are satisfied in various ways, often by hydrogen or hydrocarbon radicals. The simplest alcohol, methyl alcohol, has these other valences taken up with hydrogen atoms, i.e., CH_3OH . Many alcohols are known, but to the average reader the word "alcohol" usually means ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, also known as grain alcohol, from one of its sources. It takes its scientific name from the hydrocarbon containing the same number of carbon atoms, ethane.



Preparation of Alcohol from Ethylene. Large quantities of ethyl alcohol are now prepared from ethylene, the latter substance being obtained from petroleum. The reaction involves the taking on of water.



The process is carried out in the presence of strong sulfuric acid.

Preparation of Alcohol by Fermentation. Ethyl alcohol is prepared from sugar, or indirectly from starch, in the important process of *fermentation*. This chemical change is brought about by the catalytic action of certain large organic molecules formed during the life cycle of single-celled microorganisms known as yeasts. The molecules catalyzing the change belong to a class of compounds called *enzymes*, remarkable substances which cause chemical reactions to take place upon contact which might otherwise be exceedingly difficult or impossible to bring about in the laboratory. All living organisms manufacture enzymes of many different kinds, and the catalyzed change of sugar to alcohol is only one of a great number of such reactions.

At one time it was thought that the living organisms in which the enzymes were formed were themselves necessary for the fermentation to take place, but we now know that these are needed only to manufacture the enzymes, since the filtered liquid from yeast produces the same effect, i.e., the enzymes, passing through the filter and leaving the organisms behind, still cause fermentation.

There are various types of fermentations, produced by the action of enzymes upon organic molecules. The one now under consideration is known as *alcoholic* fermentation. When yeast is added to a solution in water of a sugar known as glucose, the enzyme *zymase*, present in the yeast, causes the chemical change



FIGURE 15.1. Molasses Fermentation Tank, Used in Obtaining Alcohol. Courtesy Monsanto Chemical Company.

of the glucose to alcohol. The starting and final products of the reaction are shown by the following equation.



While this reaction has been written as if it took place in one simple step, actually a whole series of steps is involved. Much research has been done in an attempt to learn these steps, and it begins to appear that they have been determined. Among other changes, there is apparently a transfer of phosphate radicals from the enzyme to the sugar and back again, and the intermediate formation of pyruvic acid, CH_3COCOOH .

Table sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is also converted to alcohol by the enzymes in yeast. Here another enzyme, *invertase*, causes the sucrose to take on water and split into the simpler sugars glucose and fructose, which are structural isomers.

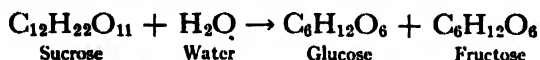


FIGURE 15.2. Distillation of Alcohol. Distilling column used in obtaining alcohol from fermented molasses. Courtesy Monsanto Chemical Company.

The glucose and fructose are then changed to alcohol by zymase as described above.

Alcohol is commonly made by fermenting cheaper carbohydrates than purified glucose or sucrose, however. Molasses is the starting product for much of our alcohol. It is mostly a water solution of sucrose. Starch from various sources, as corn, potatoes, or barley, is also used extensively. In the fermentation starch is first converted to maltose and glucose, as described in the next chapter. The United States production of industrial alcohol in 1946 was 329 million gallons.

Solutions of alcohol resulting from fermentation are under 20 per cent, since higher alcohol concentrations kill the yeast. To obtain stronger solutions fractional distillation is employed (page 316). Alcohol can be separated from water in this way to

give a concentration of nearly 96 per cent by weight, but to make *absolute* alcohol (100 per cent), other methods are required. The absolute product is made commercially by distilling the 95+ per cent product with benzene. In the resulting distillation water, alcohol and benzene come off in the early stages of the distillation, and absolute alcohol in the last stage.

Physical Properties of Alcohol. Pure ethyl alcohol is a colorless liquid having nearly the same viscosity as water (it is 1.2 times as viscous as water at room temperature). It boils at 78.3°C . and freezes at -114°C . The boiling point of ethyl alcohol is seen to be about 167° higher than that of ethane. The additional oxygen atom which distinguishes the ethyl alcohol molecule has therefore greatly affected this property, probably by causing an attraction between alcohol molecules similar to that between water molecules (page 115), in which a loose bond forms between the hydrogen atom of one molecule and the oxygen atom of another.

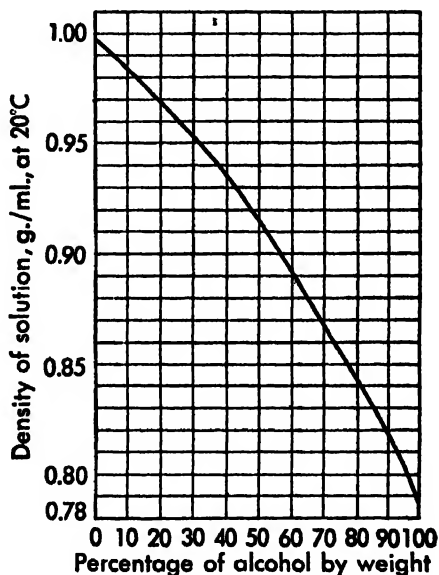
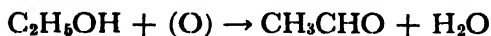


FIGURE 15.3. Densities of Alcohol-Water Mixtures.

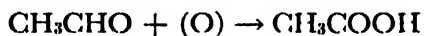
Alcohol has a density of 0.789 g./ml. at 20°C ., making it approximately four-fifths as dense as water. Alcohol is miscible in all proportions with water, and the percentage of alcohol in an alcohol-water mixture can be found by determining the density of the mixture and referring to density-composition tables available for this type of analysis. A familiar example of this procedure is in the determination of the alcohol content of car radiator fluids in the wintertime. The strength of distilled alcohol can be determined in the same manner.

Chemical Properties of Alcohol. Alcohol takes part in many chemical reactions, of which only a few will be mentioned here. Oxidizing agents convert it to *acetaldehyde*. In the equation below (O) signifies oxygen from the air or from one of a number of oxidizing agents not shown, such as potassium permanganate (KMnO_4) or potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$).



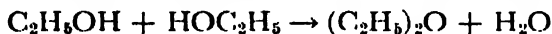
$$\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{O} \end{array}$$

Acetaldehyde has the group $-\text{C}=\text{O}$ as part of its molecule. This group characterizes all aldehydes, oxidation products of primary alcohols (alcohols of the type RCH_2OH). Acetaldehyde is a colorless, water soluble liquid which boils at only 20.2°C . It is readily oxidized further to yield *acetic acid*.



These general changes, i.e., oxidation of alcohols to aldehydes and aldehydes to acids, are important to the organic chemist.

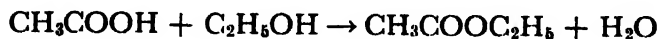
Two molecules of ethyl alcohol lose a water molecule between them when the substance is warmed with sulfuric acid, and *diethyl ether* is formed. Ethers are seen to be organic oxides of the



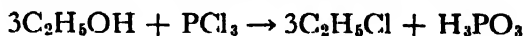
general formula R_2O , or ROR' , where R and R' are different organic groups, usually hydrocarbons, such as methyl, ethyl, etc. Diethyl ether is the "ether" so widely used in surgery as an anesthetic. Diethyl ether is highly flammable, and with a boiling point of only 34.5°C . it has such a high vapor pressure at room temperature that an explosive mixture of air and ether vapor readily forms. Those using the product should always be aware of this potential danger.

Alcohols react with acids to form *esters*. The reaction is somewhat similar to the formation of salts from acids and bases in inorganic chemistry, since a substance with a hydroxyl group (the alcohol) reacts with a substance having replaceable hydrogen atoms (the acid) to form an ester and water. If the acid em-

ployed is organic the resulting esters often have a fruity odor. Thus, in the reaction between ethyl alcohol and acetic acid, shown below, the product, ethyl acetate, smells somewhat like ripe bananas. Ethyl acetate is a colorless liquid boiling at 77°C.



Ethyl alcohol reacts with phosphorus trichloride to yield the product *ethyl chloride*. The latter is an example of an organic chloride, an important class of substances including such things as carbon tetrachloride, chloroform, DDT, para-dichlorobenzene, etc. Ethyl chloride is a colorless gas liquefying at 13.1°C.



Alcoholic Beverages. Some alcoholic beverages and their sources are given in the following table. Material allowed to ferment is at the left.

TABLE 15.1 Some Common Alcoholic Beverages

<i>Source of sugar or starch</i>	<i>Resulting beverage undistilled</i>	<i>Resulting beverage distilled</i>
GRAPES (CO ₂ retained)	Champagne	
GRAPES OR OTHER FRUIT	Wine	Brandy
APPLES	Cider	
MOLASSES		Rum
JUNIPER AND RYE		Gin
CACTUS	Colonche	
TEQUILA (Century plant)		Tequila
BARLEY, WHEAT, RYE	Beer	Brandy, Whiskey
CORN		Brandy, Whiskey
POTATOES		Brandy, Vodka
RICE	Saki	Arrack

Uses of Alcohol. Besides its use in alcoholic beverages, ethyl alcohol is employed in a number of other ways. It is an important solvent, used in the preparation of solutions such as tinctures (e.g., tincture of iodine), essences (e.g., perfumes) and extracts (such as vanilla extract). It is used to dissolve shellac, and is added to some varnishes and lacquers. It is the starting substance in the manufacture of other chemicals, such as ether and acetic acid.



It is used as a fuel, and has been proposed as a gasoline substitute in automobiles. Mixed with certain salts in gel form it is sold as "canned heat," in which the contents of the can are lit to produce a hot, blue, smokeless flame. It is often used in thermometers in place of mercury. It has the advantage

FIGURE 15.4. Closed Fermentation Tanks used in Beer Manufacture. Wort, an extract made from hops, barley, malt, rice, corn, and yeast, is allowed to ferment in these tanks for

7-9 days. The carbon dioxide evolved is saved and later put back into the product. After this treatment the wort is called beer. Courtesy Brewing Corporation of America.

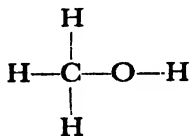


FIGURE 15.5. Bottling Tanks Used in Beer Manufacture. After fermentation beer is stored for 15-20 days, following which it is carbonated, filtered, and pumped to these government bottling tanks. From here it is transferred by hose to the bottling machines. Courtesy Brewing Corporation of America.

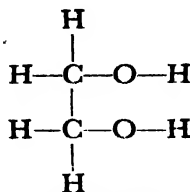
here that it freezes at $-114^{\circ}\text{C}.$, and so can be used to record the lowest temperatures found anywhere in nature on the earth's surface. Mercury, freezing at $-39^{\circ}\text{C}.$ ($-38^{\circ}\text{F}.$), is not suitable for the thermometers used in polar regions. Alcohol is also employed as a preservative, since in high concentrations it destroys the insects, bacteria, and molds which threaten biological specimens.

Several hundred million gallons of alcohol are manufactured annually for uses other than in alcoholic liquors, and to avoid the heavy tax which must be paid on beverage alcohol, all but a few million gallons is *denatured*, i.e., chemicals are added which make it unfit for drinking. Methyl alcohol is a common denaturing material. Much of the remaining, undenatured, product is used in hospitals and for scientific work.

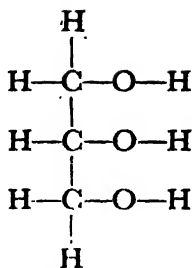
Other Alcohols. Many other alcohols are known. The formulas of three important ones are shown below. *Methyl alcohol*, prepared by combination of carbon monoxide and hydrogen, is used as an antifreeze and a solvent. It is poisonous when taken internally. *Ethylene glycol* is an example of a *dihydric* alcohol (one containing two hydroxyl groups). Made from ethylene, it is used as an antifreeze, being superior because of its high boiling point ($197.4^{\circ}\text{C}.$), and consequent low rate of vaporization. *Glycerine*, obtained from fats and oils, has three hydroxyl groups. It is used in making synthetic resins which are employed in some protective coatings. It is utilized as an antidrying agent, an antifreeze, and in lotions, cosmetics, and medicines. This substance is now also made as a petrochemical, being prepared from propylene.



Methyl alcohol



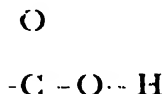
Ethylene glycol



Glycerine or glycerol

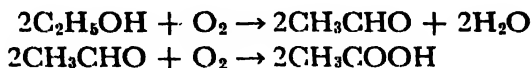
ACETIC ACID

An acid in organic chemistry is usually a substance whose molecule contains the *carboxyl* group,



Formic acid, HCOOH , is the simplest organic compound containing this group. The hydrogen atom in the carboxyl group is able to ionize to some extent, i.e., to leave the molecule as a hydrogen ion, which is why molecules containing this group have acid properties.

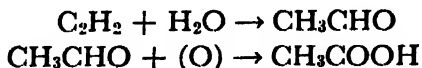
Preparation and Occurrence. One of the properties of alcohol mentioned in the previous section was its reaction with oxidizing agents to form acetaldehyde (page 356), after which the latter substance readily oxidized further to acetic acid. This process goes on very widely in nature, catalyzed by enzymes made during the growth of certain bacteria of the genus *aceto-bacter*. The latter are present in the air, and in great numbers in the "mother of vinegar" liquid added to alcoholic solutions in the making of vinegar. The souring of wine or cider after it has been allowed to stand in contact with the air is caused by these bacteria. The chemical changes are shown below. Not all alcoholic liquids are so affected.



Liquors higher in alcoholic content, such as port, sherry, whiskey, etc., are not soured because the bacteria which produce the enzymes cannot grow in the stronger solution. Pure alcohol dissolved in water is also not oxidized, even in dilute solution, because the microorganisms need the nitrogenous impurities and the salts which are present in fruit juices and other plant liquids in order to grow.

Vinegar. The product which results when the alcohol in such liquids as cider is oxidized to acetic acid is *vinegar*. The process is hastened by allowing the slightly warm alcoholic liquid (30°C.) to trickle over wood shavings, and at the same time forcing air through the mass from below. Oxidation under these conditions is rapid because the liquid has ample opportunity to absorb oxygen and the surface of the chips offers a good breeding place for the bacteria producing the enzymes. The resulting vinegar is quite dilute—4 to 6 per cent—and contains only one or two acetic acid molecules for every hundred water molecules. It also contains small amounts of many other substances—including esters, carbohydrates, nitrogenous compounds and acids other than acetic—which help give the product the odor and taste characteristic of that kind of vinegar. Synthetic vinegars are also sold. These are made by diluting strong acetic acid with water, and adding coloring matter and other substances in an attempt to duplicate the properties of the natural products.

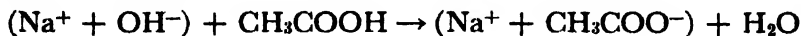
Concentrated Acetic Acid. Acetic acid is an important compound in other ways than as a component of vinegar. It is now made in concentrated form by several different methods, the most recent being from the hydrocarbon acetylene (page 338). This reacts with water in the presence of a catalyst to form acetaldehyde; the latter is then oxidized to acetic acid.



Pure acetic acid boils at 118°C. and freezes at 16.7°C. It has a powerful vinegar-like odor. Laboratory temperature may fall

below the freezing point of pure acetic acid, causing the substance to solidify to ice-like crystals. For this reason, the pure product is sometimes called glacial acetic acid.

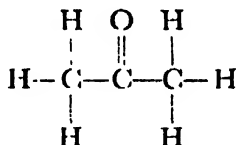
The substance reacts with bases to form salts. Thus, with sodium hydroxide:



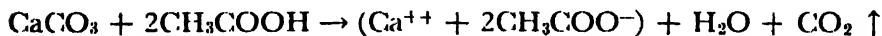
These salts themselves take part in well-known chemical reactions. For example, sodium acetate yields methane when heated with a base (page 330). Calcium acetate, when heated, gives the important chemical *acetone*.



This is one of a class of compounds known as *ketones*, and characterized by the general formula R_2CO or $\text{RR}'\text{CO}$. The structural formula for acetone is shown below. It is an important solvent.



Acetic acid reacts with carbonates, causing evolution of carbon dioxide. With calcium carbonate, for example:



Cleopatra is said, by Pliny, to have enjoyed drinking a concoction made by dissolving pearls (calcium carbonate, chiefly) in vinegar. She therefore apparently had a liking for dilute, carbonated calcium acetate solution.

Esters are formed when acetic acid reacts with alcohols in the presence of a dehydrating agent (page 356).

Acetic acid has a number of uses besides that in vinegar. It is employed in the manufacture of the pigment "white lead," in a process where metallic lead is converted to lead acetate which in turn is changed to basic lead carbonate, the pigment. Other metallic acetates are important as pigments, mordants, and insect-



FIGURE 15.6. A Use for Acetic Acid. Lead buckles are corroded with acetic acid and carbonic acid in the Dutch process for making white lead, an important paint pigment. Courtesy The Sherwin-Williams Company.

ticides. Acetic acid is used to make acetate esters (perfumes, cellulose acetate plastic, and fiber, etc.) and in the manufacture of acetone. It is a common reagent in the laboratory, being utilized in most cases when a weakly dissociated acid is required.

Self Study Questions

1. What group of atoms characterizes alcohols? Write the formulas for *n*-butyl and *n*-hexyl alcohol. How many isomeric alcohols can be

derived from *n*-heptane? Name $\text{CH}_3-\text{C}-\text{CH}_3$ *tertiary propyl alcohol*

Handwritten notes: OH groups (with arrow pointing to the OH group in the structure), $\text{C}_4\text{H}_9\text{OH}$, $\text{C}_6\text{H}_{13}\text{OH}$, 6 (under the question), and *tertiary propyl alcohol* (next to the structure).

$$\begin{array}{c} \text{H} \\ | \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ | \\ \text{O} \\ | \\ \text{H} \end{array}$$

2. What enzyme causes the fermentation of glucose to alcohol? Write the equation for the change, showing only the initial and final substances.

3. What additional enzyme is needed to obtain alcohol from sucrose? Write the equation for the reaction.

4. How is the dilute alcohol solution which results from fermentation concentrated? How is absolute alcohol prepared?

5. Account for the fact that the boiling point of ethyl alcohol is 167° higher than that for ethane.

6. What simple method can be used to show the concentration of alcohol in an alcohol-water mixture? What is the percentage by weight of alcohol in a mixture having a density of 0.855 (Figure 15.3)?

7. What is an aldehyde? Note that these are often named from the acid to which they can be oxidized. What, then, is the formula for formaldehyde? Write equations for the oxidation of ethyl alcohol to acetaldehyde and of the latter to acetic acid.

8. How is diethyl ether obtained from ethyl alcohol? Write an equation. What precaution should be observed in using this substance?

9. What is an ester? Write the equation for the formation of ethyl propionate from ethyl alcohol and propionic acid ($\text{C}_2\text{H}_5\text{COOH}$)

10. Show by an equation how ethyl chloride can be obtained from ethyl alcohol.

11. Give six uses for alcohol besides its use in alcoholic liquors.

12. What is the carboxyl group? What class of substances contains this group? What is the simplest molecule containing this group?

13. Write the structural formula for acetic acid. Which hydrogen ionizes in water solution?

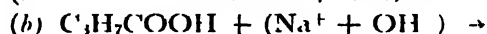
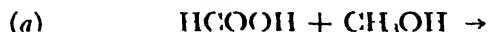
14. Explain the formation in nature of acetic acid from ethyl alcohol. Include equations.

15. Show by equations how acetic acid can be prepared from acetylene.

16. Illustrate with equations three chemical changes in which acetic acid takes part.

17. What is glacial acetic acid? Name four uses of acetic acid.

18. Complete the following equations.



19. Assuming the yield to be 75 per cent of theory,¹ calculate the weight of butyl propionate that can be prepared by the reaction between 100 grams of butyl alcohol ($\text{C}_4\text{H}_9\text{OH}$) and excess propionic

¹ Very few organic reactions give 100 per cent of pure, isolable product, because of competing reactions, equilibrium factors, and difficulties encountered in separating the product.

acid ($\text{C}_2\text{H}_5\text{COOH}$). Butyl propionate has a density of 0.883 g./ml. What, then, will be the volume of the product?

Answer: 132 grams, 149 ml.

20. Six types of organic compounds made up of carbon, hydrogen, and oxygen have been mentioned in this chapter. See if you can name them.

XVI

The Carbohydrates

The most plentiful substances formed by growing plants are the sugars, starches, and celluloses, known collectively as the *carbohydrates*. The name is a contraction of the expression "carbon hydrate," since most carbohydrates have hydrogen and oxygen present in their molecules in the ratio by atoms of two to one, as in water, and their formulas can therefore be written as if they were indeed hydrates of carbon. Thus, table sugar, $C_{12}H_{22}O_{11}$, could be written $C_{12} \cdot (H_2O)_{11}$. However, in a true hydrate water is present as such in the crystals, whereas in carbohydrates, the hydrogen and oxygen are present in units smaller than water molecules, i.e., as the groups $-H$, $-O-$, and $-OH$.

The Carbohydrate Building Unit. The carbohydrates differ tremendously in the size of their molecules, from the sweet, water soluble sugars to the tasteless, highly insoluble celluloses. But most of them, at least those most important to man, have the building unit $-C_6H_{10}O_5-$ in common. This unit exists in various isomeric forms, each as the structure shown below, or something rather similar.

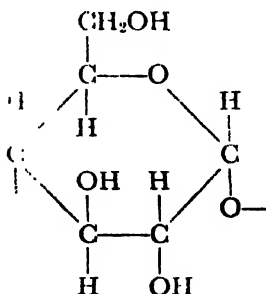
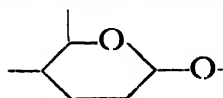




FIGURE 16.1. Dextrose Drier. Hot air is employed and the drier is tilted to bring dextrose to the finishing end. Courtesy Corn Industries Research Foundation.

This unit will henceforth be referred to as the $-\text{C}_6\text{H}_{10}\text{O}_5-$,

or the  unit. One or two of these $-\text{C}_6\text{H}_{10}\text{O}_5-$

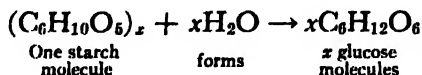
rings make up the molecules of most soluble sugars. Most dextrin molecules probably consist of several dozen rings joined together, while starch molecules contain hundreds, and perhaps in some cases thousands of such rings. Largest of all, on the average, are the giant cellulose molecules, probably made up of thousands of these rings as they occur in nature, hence having molecular weights going up to a million or more.

Let us now consider five common carbohydrates in the order of increasing complexity: glucose, sucrose, the dextrans, starches, and celluloses.

GLUCOSE

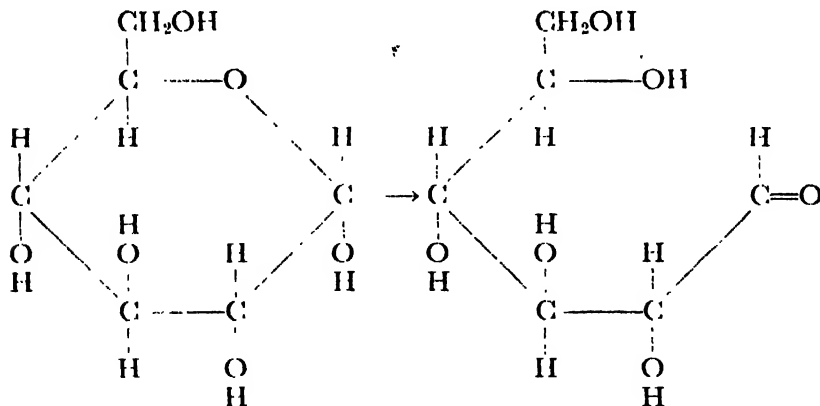
Occurrence and Preparation. The simple sugar glucose is also known as dextrose and as grape sugar, the last name being because grapes contain more of the sugar than most fruits. The

substance is made commercially from starch, and in this country chiefly from cornstarch. The large molecules of the latter, when heated with water in the presence of hydrochloric acid, split up, take on water and form glucose.



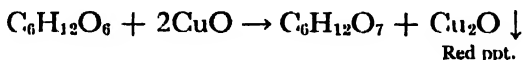
Structures of Glucose. Glucose is thought to exist chiefly as closed-chain molecules which are similar to the $\text{C}_6\text{H}_{10}\text{O}_5$ ring shown on page 366 except that the two free valences of the latter are satisfied with a hydrogen and a hydroxide group, i.e.,

$\text{C}_6\text{H}_{12}\text{O}_6$ or $\text{HO}-\text{C}_6\text{H}_9\text{O}_5-\text{OH}$. However, in solution the glucose rings in part open up, by a movement of hydrogen from one oxygen atom to another, as shown below. The two forms are thought to be in equilibrium with each other. The open chain structure which results was regarded at one time as the only formula for glucose.



Properties of Glucose. Pure, anhydrous glucose forms colorless crystals melting at 146°C . A water solution of the substance made from cornstarch is of commercial importance and is known as corn syrup. This solution is not pure, since it also contains another sugar, maltose, and dextrins. When starches or sugars

are eaten they take up water and largely change to glucose as did starch on the previous page. The glucose passes through the intestinal wall into the blood stream, and is eventually oxidized. It is normally present in the blood to the extent of approximately 0.1 per cent. In the pathological condition known as *diabetes*, the body is unable to use up glucose at a normal rate. Its concentration in the blood increases, and it begins to filter through the kidneys into the urine. One of the symptoms of diabetes, then, is the presence of glucose in the urine, where it can be detected by its reducing action upon colloidal, hydrous cupric oxide (Benedict's or Fehling's solution). When glucose is present a red precipitate of cuprous oxide forms, as shown in the following simplified equation.



This test is not specific for glucose, since some other sugars also reduce Fehling's or Benedict's solution; the group goes under the general heading of *reducing* sugars.

Optical Isomers. When plane polarized light¹ is transmitted through an ordinary glucose solution *the plane of vibration of the light is turned clockwise, or to the right*. Other sugars also cause a turning of light in this way, sometimes to the right and sometimes



FIGURE 16.2. Corn Syrup Entering Cooler. After its preparation from starch the corn syrup has been neutralized and concentrated prior to this stage. Courtesy Corn Industries Research Foundation.

¹ Light vibrates transversely to its line of propagation. When these transverse vibrations are in one plane only which includes the line of propagation, the light is said to be plane polarized.

to the left, and many other organic compounds do likewise. Such substances are said to be optically active. It has been found that this property is exhibited whenever molecules exist in which a carbon atom has four different groups surrounding it in space.

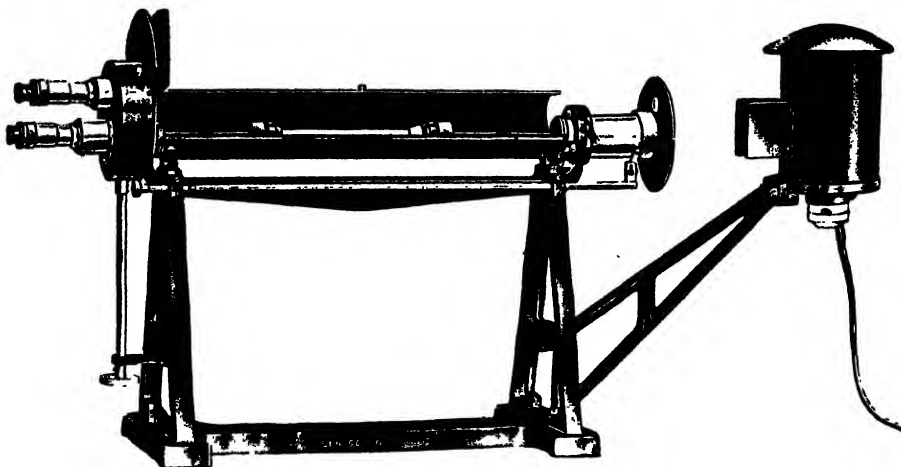


FIGURE 16.3. Polarimeter. Light source at right. Light is polarized, then passed through tube containing solution of optically-active substance. Angle of rotation of emerging light is found by mechanism at left. Courtesy Central Scientific Company.

Each of the isomers which results from this type of molecule (*optical isomers*) is found to turn plane polarized light in a characteristic manner. Since ordinary glucose turns plane polarized light to the right it is sometimes called dextrose, from the Latin word "dextra," meaning the right hand. Optical activity is useful in analysis, since compounds which exhibit the property can be qualitatively and quantitatively determined from the direction and degree of light rotation. The instrument used for the purpose is known as a polarimeter.

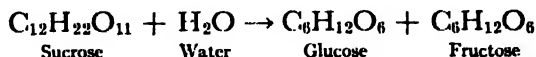
SUCROSE

Common table sugar, or sucrose, consists of molecules which are made up of two of the $\text{—C}_6\text{H}_{10}\text{O}_5\text{—}$ carbohydrate building units mentioned earlier, plus a hydrogen and hydroxide radical to satisfy the remaining two free valences. Sucrose therefore has

the formula $C_{12}H_{22}O_{11}$. The two $-C_6H_{10}O_5-$ building units in sucrose are isomers of each other, with different structures.

Occurrence; Preparation. Sucrose is formed during the growth of many plants, but the chief sources of commercial importance are sugar cane and sugar beets. These two plants are approximately one sixth sugar. Extraction of the sugar from cane or beets is accomplished by allowing water to come into intimate contact with the plant juices, the plants being crushed or chopped to aid in this process. The sugar solution so formed may be evaporated at once to give brown sugar, or the solution of the latter may be purified further, by adsorption and precipitation of impurities, and by filtration, to give a colorless syrup. This is evaporated under reduced pressure, to keep temperature low and hence lessen decomposition. Evaporation is not carried to completion; the liquid which remains is sold as *molasses*. The sugar crystals formed during the evaporation are kept small by agitation, and are then dried in a centrifuge. They constitute the familiar sugar seen in the home. A quiet evaporation is sometimes allowed to take place, giving large sugar crystals (rock candy).

Properties of Sucrose. Sucrose is not a reducing sugar. Its solutions turn plane polarized light to the right, like glucose, only more strongly so. When warmed with dilute acid solutions sucrose takes on water and forms two simpler sugars, glucose and fructose.



This process is called *inversion*, because of the change which takes place in the rotation of plane polarized light. After the reaction the latter is turned counterclockwise, in spite of the formation of the dextrorotatory glucose, because of the strong laevorotation (turning to the left) produced by the fructose. The mixture of sugars formed in this way is called *invert sugar*. Honey contains a considerable amount of invert sugar. Chemicals furnished by



(a)



(b)

FIGURE 16.4. Sources of Sucrose. (a) Sugar cane. (b) Sugar beets. Note the mechanization which is occurring in this industry. Courtesy Sugar Research Foundation, Inc.



FIGURE 16.5. Cane Sugar Manufacture. Sugar cane is being broken up here. The process is so effective that 98% of the juice is able to be extracted. Courtesy Sugar Research Foundation, Inc.



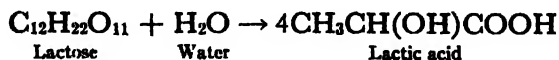
FIGURE 16.6. Table Sugar. Sucrose crystals are made in the crystallizing tanks shown in the middle of the picture. The mixture is then centrifuged at the lower level, causing the impure solution to be thrown off while sugar crystals are caught in wire mesh baskets. Courtesy Sugar Research Foundation, Inc.

the bees cause the inversion of the sucrose which these insects collect from flowers. Invert sugar is less sweet than sucrose.

When sucrose is heated to 170°C . it turns brown, because of a partial decomposition, and the familiar substance *caramel* is formed.

Isomers of Sucrose. Two other disaccharides (two-ringed molecules), isomeric with sucrose, should be mentioned. One is *lactose*, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, with two $-\text{C}_6\text{H}_{10}\text{O}_5-$ rings much more nearly alike than those in sucrose. It is the sugar present in milk. Cow's milk contains about 5 per cent of the substance. It is neither as sweet nor as soluble as sucrose, and at low temperatures, as in the making of ice cream, it may crystallize out to give the granular texture sometimes found in that product. To prevent such large crystal formation ice cream manufacturers

commonly add gelatin, which keeps the lactose crystals small. When milk sours, it is because the lactose is chemically changed to lactic acid by microorganisms which get into the milk from the air.



The other disaccharide is *maltose*, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, whose molecule is made up of two of the carbohydrate units shown on page 366.

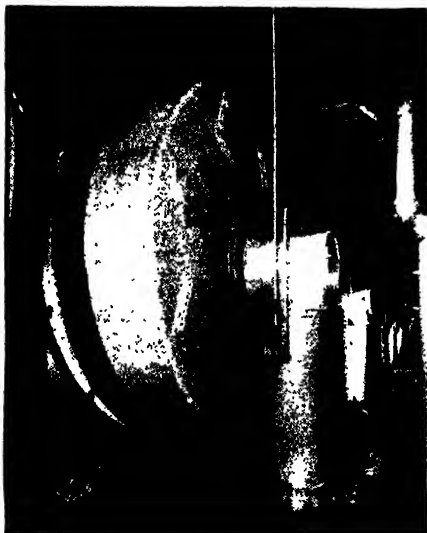


FIGURE 16.7. Malting Drums. Germination of barley in these drums produces malt, which contains enough diastase to convert as much as ten times its own weight of additional starch to sugars and dextrins. Gearing is for drum rotation to promote uniform aeration and prevent matting of the sprouting rootlets. Courtesy The Columbia Malting Company.

The common source of maltose is starch. When the latter is acted upon by *diastase*, an enzyme in sprouting grain, it is largely converted to maltose and dextrin. Another enzyme found in the saliva, *ptyalin*, also converts amylose starch (page 376) to maltose, and this accounts for the sweetness which is noticed when starch is chewed in the mouth for long periods of time.

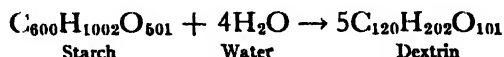
Malt. Sprouting grain contains maltose and dextrin, made from the starch present because of the catalytic action of diastase. The diastatic mixture obtained by drying grain after it has been allowed to sprout (usually barley) is called *malt* (Figure 16.7). Since it contains diastase it has the power of causing conversion of additional starch to maltose and dextrin. This process is carried out commercially with starch from such sources as corn, rye, barley, rice, and potatoes. The maltose-dextrin mixture which results is used in foods, e.g., malted milk, candy, and as the starting product of malt liquors such as beer and ale. These are

made by treating malt with yeast, the enzymes of which cause conversion of maltose to alcohol as described in the last chapter.

THE DEXTRINS

The remaining carbohydrates to be discussed are made up of chains of carbohydrate building units like that shown on page 366. But unlike glucose or sucrose, the number of units in the molecules of these more complicated carbohydrates is not constant. There is furthermore some uncertainty as to what the number is, since this is difficult to determine experimentally. So in speaking of these substances it should be kept in mind that there is a range of molecules in each case, shown by use of plurals, i.e., dextrans, starches, and celluloses. It appears that in many dextrin molecules there are a few dozen $\text{—C}_6\text{H}_{10}\text{O}_5\text{—}$ building units, while those of the starches may well contain hundreds, and the celluloses thousands of these units.

The dextrans are made from starch, by a breaking down of the latter molecules by heat, into simpler units. A taking up of water accompanies the process, to furnish hydrogen and hydroxide radicals for the free valences which result when the bond is broken between the $\text{—C}_6\text{H}_{10}\text{O}_5\text{—}$ units. If the assumption be made that starch with 100 carbohydrate building units forms dextrin with 20 such units, then the equation for the change would be:



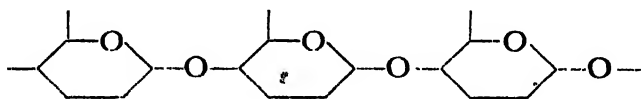
Dextrans are also formed by heating starch with dilute acids, and by the action of the enzyme diastase upon starch, as described earlier.

A dextrin suspension in water forms a sticky adhesive. This is the substance used on postage stamps, labels and envelopes. The dextrans are used in textile sizing, and as a thickening agent for some fluids. The dextrans are present in many foods, including corn syrup, bread crust, honey, beer, ale, and malt. Dextrin is named, like the simpler dextrose, because in solution it turns a beam of plane polarized light to the right.

STARCHES

The starches are substances of high molecular weight produced by growing plants and used as a carbohydrate reserve. They are present in large amounts in cereals, such as corn, and roots, such as potatoes. They are also formed in unripe fruit, and are partially changed to sugar as the fruit ripens, giving it a sweet taste. The starch in plants occurs in the form of granules, large enough to be visible under the microscope (Figure 16.8). The source of a given sample of starch can often be determined by noting the size and shape of its granules.

Starch granules appear to consist of two kinds of starch. The outer part is made up of branched chains of $\text{—C}_6\text{H}_{10}\text{O}_5\text{—}$ building units containing from 300 to several thousand of the latter. It is insoluble in hot water. The inner portion of the granules consists of smaller, unbranched chains, containing from 60 to approximately 300 $\text{—C}_6\text{H}_{10}\text{O}_5\text{—}$ units. It forms a suspension in hot water. A portion of the chain appears as shown below.



Starch gives an intense color when it comes in contact with iodine, particularly the unbranched molecules (amylose), which form a blue complex. This color is so pronounced that a mere trace of iodine can be detected by adding starch. The complex appears to be a combination of starch, iodine, iodide ion, and water. The larger, branched-chain starches (amylopectin) are also colored by iodine, but violet or red-violet rather than blue.

The chief use of starch is as a food. It is the most important carbohydrate in our diet, consumed in larger quantities than sugars or dextrans. Starch is the starting material used for making much of our dextrin, maltose, glucose, and alcohol. It is also employed as a stiffening agent for cloth, in the familiar process of "starching."

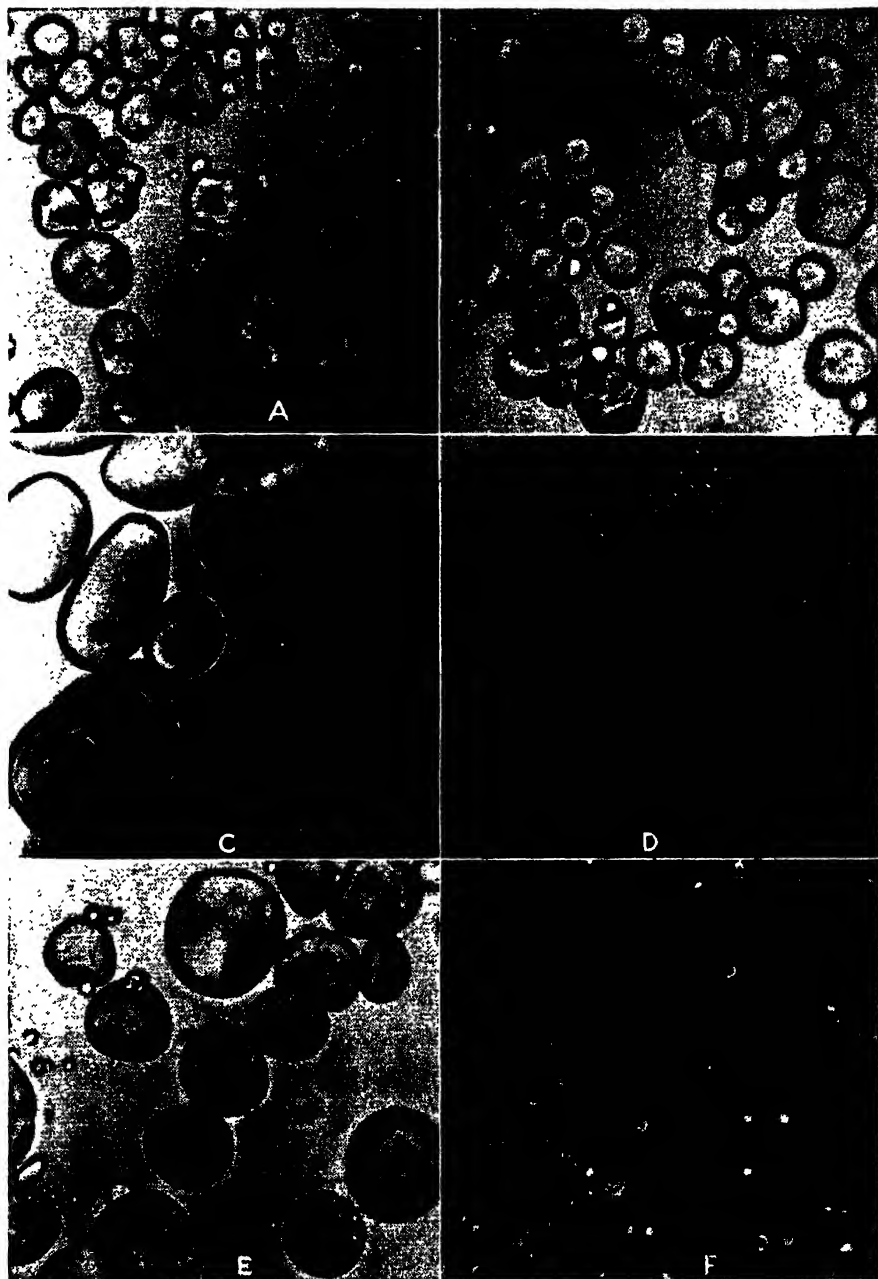


FIGURE 16.8. Starch Granules, Magnified. (a) Corn, (b) Tapioca, (c) Potato, (d) Rice, (e) Rye, (f) Wheat. Courtesy Corn Industries Research Foundation.

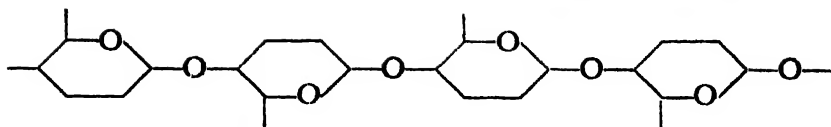


FIGURE 16.9. Starch Filter. Starch suspension comes into the bed of the filter and is picked up on the revolving drum by means of a partial vacuum within the drum. Courtesy Corn Industries Research Foundation.

THE CELLULOSES

Cellulose is not a food as far as man is concerned, since he does not have the necessary enzymes to break it down into molecules small enough for assimilation. However, many microorganisms can digest it, as can also cows and other ruminants, because of the presence of some of these microorganisms in their digestive tracts. It is the chief carbohydrate produced in plants, made by them as a stiffening agent for cell walls and plant structures in general. Cellulose molecules consist of unbranched chains of $\text{—C}_6\text{H}_{10}\text{O}_5\text{—}$ building units. There may be as many as 10,000 of these units in one cellulose molecule, as it occurs in nature. However, in regenerated cellulose, and in the various cellulose derivatives made from the natural product, these long chains are split into much smaller molecules which contain hundreds rather than thousands of $\text{—C}_6\text{H}_{10}\text{O}_5\text{—}$ units.

The arrangement of $\text{—C}_6\text{H}_{10}\text{O}_5\text{—}$ units is different in cellulose than in starch. Compare the partial structure shown below with that for starch given on page 376.



Uses of Cellulose. Cellulose is now treated in many ways to give ^{cellulose} products (useful) to man. The chief sources of the substance are cotton and wood. Both of these contain impurities which must be removed if pure cellulose is desired. Cotton fibers are covered with a wax which must be dissolved in a solvent. Wood contains a variety of intercellular matter, including resins and lignin. In the manufacture of pulp for paper these impurities are reduced or removed in various ways, but generally either by grinding the fibers loose or by cooking them in hot liquors containing sodium sulfite.

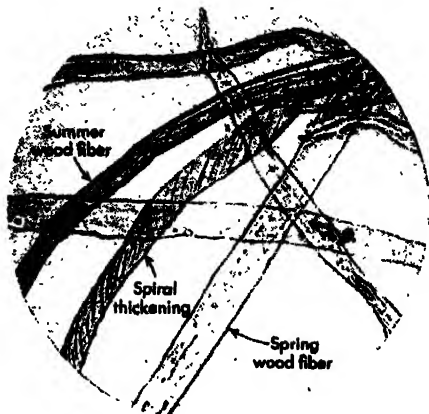


FIGURE 16.10. Cellulose Fibers from Pine Wood. Magnified two hundred times. Courtesy West Virginia Pulp and Paper Company.

Combinations of chemical and mechanical treatment under the name of "semi-chemical processes" are also rapidly developing.

Some forms of paper are essentially pure cellulose, e.g., ashless filter paper, but most either retain part of the intercellular matter or carry added substances, such as starch, chalk, or even latex, according to the specific characteristics desired. Immersion of paper in cold, concentrated sulfuric acid gives a ^{similar} product similar to parchment in feel and durability. It is often called *vegetable parchment*. The surface of paper so treated is waterproof. By protracted beating of cellulose fibers and chemical treatment, many interesting special qualities may be obtained, such as transparency, flexibility, or impermeability to grease and odors.

When cellulose comes in contact with nitric and sulfuric acids, hydroxyl groups at several spots in the molecule are replaced by $-\text{NO}_2$ radicals, and serviceable substances known as cellulose



FIGURE 16.11. Cotton Linters, a Common Source of Cellulose. Here the linters are being put into an acetator to be made eventually into acetate rayon. Courtesy E. I. du Pont de Nemours & Co.

nitrate are formed. Moderate nitration produces *pyroxylin*, used in collodion, lacquers (e.g., Duco), photographic film, celluloid, etc. A greater degree of nitration gives the product gun cotton, used as an explosive.

An important group of industries has developed in which cellulose is put into a colloidal suspension by chemical treatment and then precipitated out in desired forms. The regenerated cellulose may be in the form of a thread, as in *rayon*, or as sheets, like *cellophane*.

Cellulose acetate is another plastic product made from cellulose. It is formed by action of acetic anhydride. Cellulose acetate is used in photographic film, being less flammable than cellulose nitrate. It also finds use in the insulation of wire, and is made into thread to give another type of rayon.

When cellulose is treated with sodium hydroxide solution and then washed with water, it takes up water, forming a hydrated product which is smoother, softer, and more lustrous than ordinary cellulose. Cotton so treated is called *mercerized cotton*.

Self Study Questions

1. What is the etymology of the word "carbohydrate"?
2. Draw the structure of the most common carbohydrate building unit. Is this a molecule? Explain.
3. How does a glucose molecule differ from this carbohydrate building unit?
4. How is glucose prepared commercially? Does it exist in nature?
5. Show what change takes place when glucose assumes an open chain structure.
6. What is a reducing sugar? How are these detected? What weight of cuprous oxide could theoretically be produced by action of one gram of glucose upon excess Fehling's solution?
7. Glucose is also called dextrose. Account for the latter name.
8. How does the structure of table sugar, sucrose, differ from that of glucose? What names are used to distinguish sugars whose molecules contain one carbohydrate building unit from those whose molecules contain two of these units?
9. What are the two chief sources of sucrose? How is this sugar prepared in pure form? What steps in the manufacturing process account for rock candy? Molasses? Brown sugar?
10. What is meant by optical activity? Explain the terms inversion and invert sugar.
11. What sugar is present in milk? Explain how the souring of milk and the granulation of ice cream are caused by this sugar.
12. What sugars result when starch is (a) heated with dilute hydrochloric acid, (b) treated with the enzyme diastase? What is malt?
13. Is dextrin a specific substance? Explain. How are dextrins made?
14. How do the starches occur in nature? What two types of starch molecules exist? What is the test for starch?
15. The $\text{—C}_6\text{H}_{10}\text{O}_5\text{—}$ carbohydrate building units are joined together differently in starch than in cellulose. Describe the difference.
16. What are the chief sources of cellulose? Give an example of a product that is essentially pure cellulose.
17. What is vegetable parchment? How is it made?
18. What chemical change takes place when cellulose is treated with nitric acid in the presence of sulfuric acid? Give the names of some important products which result from this change.

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19. What is regenerated cellulose? Give examples of some familiar products made from it.

20. How is cellulose acetate prepared? What are some of its uses?

21. What is mercerized cotton? How does it differ from ordinary cotton?

22. Calculate the molecular weight of a cellulose molecule which contains 10,000 carbohydrate building units.

Answer: 1,621,400.

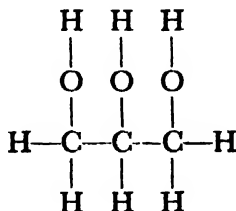
XVII

Fats; Proteins

FATS AND FATTY OILS

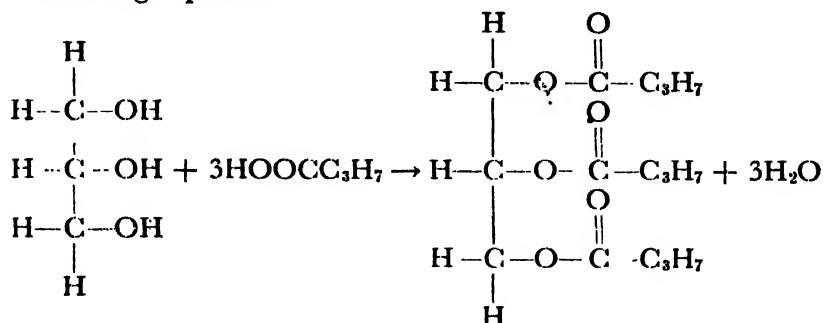
Solid and liquid fats are an essential part of our food, and in experimental animals at least it has been demonstrated that life cannot be maintained with a diet which is entirely free from fats or certain of the acids obtained from hydrolysis of fats. Plants, on the other hand, are able to form fats from carbon dioxide and water, probably in a process which first involves carbohydrate synthesis. Fats are our most concentrated form of food, since a given weight of fat upon oxidation in the body yields over twice as much energy as the same weight of protein or carbohydrate.

Composition of Fats. Fats and fatty oils are *esters* (page 356), undoubtedly formed in living plants and animals by the reaction between acids and the alcohol *glycerine*. The latter, whose structure is shown below, apparently goes into the forma-



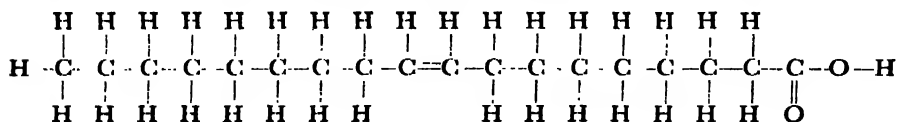
tion of all fats, whereas a great variety of acid radicals occurs, representing at least three dozen different acids. These acids are monobasic, i.e., they have but one carboxyl (—COOH) group per molecule. The differences are in the size of the mole-

cule and in the degree and position of unsaturation (page 328). The simplest ester found in fats is glyceryl butyrate, formed from glycerine and butyric acid. This ester is one of the components of butter. Its formation from glycerine and butyric acid is shown in the following equation:



Acids Obtained from Fats. Saturated acids containing an even number of carbon atoms, from butyric acid ($\text{C}_3\text{H}_7\text{COOH}$) all the way to cerotic acid ($\text{C}_{25}\text{H}_{51}\text{COOH}$), have been obtained by hydrolysis of fats. These acids are present as glyceryl esters in the fats, like the glyceryl butyrate shown above. Lauric acid ($\text{C}_{11}\text{H}_{23}\text{COOH}$), palmitic acid ($\text{C}_{15}\text{H}_{31}\text{COOH}$) and stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$) are probably the most common. Practically all of these saturated acids are members of the homologous series which starts with formic and acetic acids.

Besides the saturated acids, the radicals of many unsaturated monobasic acids appear as components of fatty oils. The commonest is the oleate radical of oleic acid, shown below.



It is seen to be similar to stearic acid except for the one double bond and the consequent deficiency of two hydrogen atoms.

The acid components of fats and fatty oils determine their properties. The melting point, for example, depends upon the molecular weight of these acids, and particularly upon the degree of unsaturation, since double bonds lead to esters with a lower



FIGURE 17.1. Extraction of Vegetable Oil. A plant for obtaining vegetable oils by the solvent extraction method from cottonseed and soya beans. Courtesy The Procter & Gamble Company.

melting point. Products which are solid at room temperature (fats) have a high proportion of glyceryl esters of saturated acids, such as glyceryl palmitate or stearate, while those which are liquid at room temperature (fatty oils) have more of the unsaturated esters. An interesting observation is that the melting point of the fat seems to depend upon its temperature of formation. Warm-blooded animals tend to make higher melting fats, as for example the beef tallow formed by cattle, while plants, with temperatures close to those of their surroundings, form the lower melting fatty oils, such as olive oil or linseed oil.

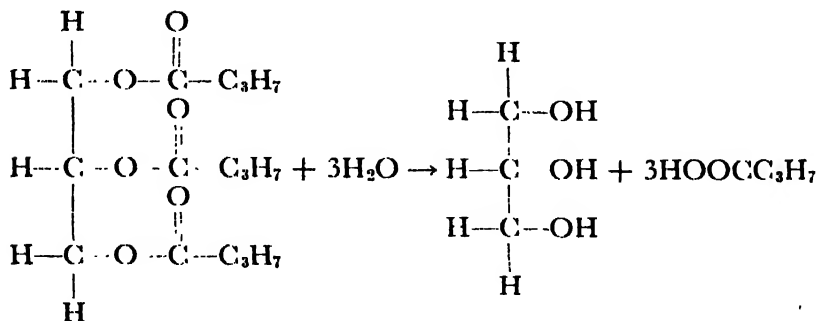
While chemists like to think in terms of pure glyceryl esters such as the laurate or stearate, actually all fats and fatty oils are mixtures of these esters, and sometimes very complicated mixtures. Butter, for example, contains esters of at least 14 different acids. Furthermore, the mixing usually extends right down to the molecule itself, so that the three acid radicals attached to the glyceryl radical may be those of two or even three different acids.



FIGURE 17.2. Hydrogenation of Oils. In these tanks vegetable oils are hydrogenated or hardened by treating them with hydrogen in the presence of a catalyst. Courtesy The Procter & Gamble Company.

Some Common Fats. Beef tallow is chiefly a mixture of glyceryl oleate, palmitate, and stearate in that order of abundance. It is among the highest melting fats known in nature. Leaf lard is rather similar in composition. It is sometimes hydrogenated (treated with hydrogen) to remove some of its unsaturated components. This improves its keeping qualities. Butter is a very complex mixture of glycerides ranging from the butyrate to that of arachidic acid ($C_{19}H_{39}COOH$). When butter becomes rancid it is due in part to the hydrolysis of glyceryl butyrate to glycerine and butyric acid.

The latter largely accounts for the unpleasant odor and taste of rancid butter.



Glyceryl butyrate + water \rightarrow glycerine + butyric acid

Some Common Fatty Oils. Olive oil is perhaps the purest form of glyceryl oleate found commonly in nature. It contains approximately 80 per cent of that ester, and smaller amounts of glyc-

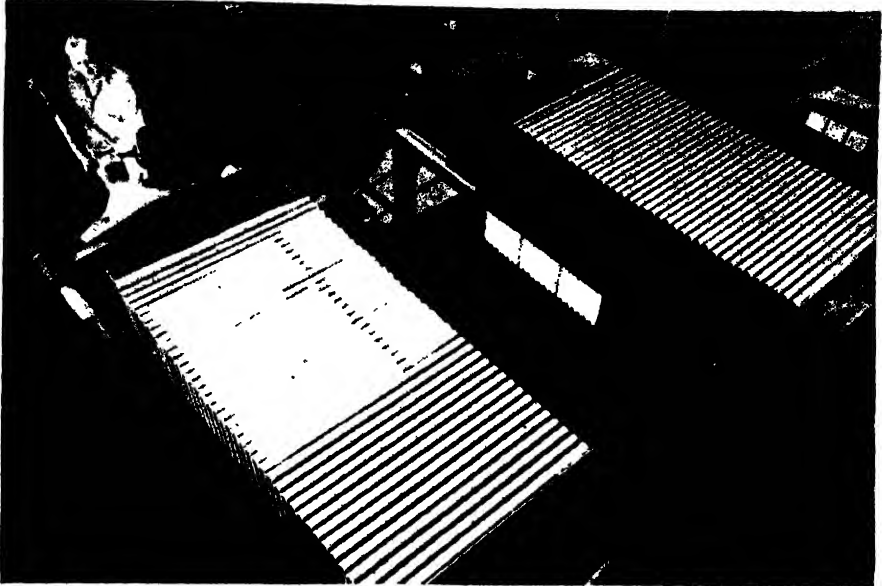
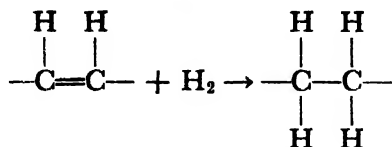


FIGURE 17.3. Purification of Hydrogenated Oil. These are filter presses for removing bleaching clay and the catalyst used in hydrogenation of vegetable oil. Courtesy The Procter & Gamble Company.

eryl palmitate, stearate, and linoleate. Coconut oil is about half glyceryl laurate, with smaller amounts of some half dozen other esters. This material and other nut oils are used in the making of lauryl alcohol, $C_{12}H_{25}OH$, important in the synthetic detergent field (page 512). Cottonseed oil, chiefly glyceryl oleate and linoleate, is one of the main sources of synthetic fats prepared by hydrogenation, described below. Linseed oil is mainly glyceryl linoleate. The last two oils, and particularly the latter, are known as “drying” oils, because upon exposure to the air they form solid films. This is due to the presence of glyceryl linoleate, an unsaturated substance with six double bonds in its molecule (page 493) which absorbs oxygen and polymerizes, changing from a liquid to a solid.

Hydrogenation of Fatty Oils. It is possible to bring about a chemical combination between an unsaturated fatty oil and hydrogen. When this is done the double bonds which make the oil unsaturated are converted to single bonds, as shown

below and the oil changes from a substance liquid at room temperature to a solid fat. This process, known as *hydrogenation*, is used



Hydrogen adds on to the double bonds of liquid fatty oils in the presence of a nickel catalyst to form saturated, solid fats.

on a large scale to convert cottonseed and other unsaturated oils to more valuable cooking fats and margarines which compete with



FIGURE 17.4. Purification of Hydrogenated Oils. A deodorizer in which hydrogenated oils are steam distilled under vacuum to remove volatile substances which give vegetable oils their natural flavor and odor. Deodorizing gives the oils a bland flavor and makes them practically odorless. Courtesy The Procter & Gamble Company.

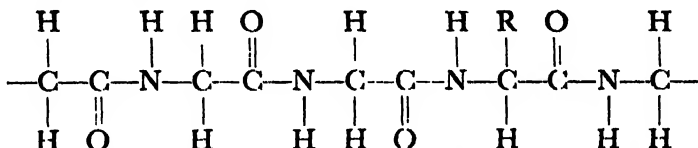
butter and other natural products. If a butter substitute is desired the hardness of the product must be adjusted to approximately that of butter, by mixing hydrogenated fats or natural fats with oils. The synthetic product is white, hence a yellow dye is added to give it the color of butter. It is also sometimes churned with milk or buttermilk to produce a flavor closer to that of butter.

PROTEINS

Proteins are indispensable substances present in many foods, particularly meats, eggs, milk, and plant seeds (peas, beans, grains, etc.). They are necessary in the diet of animals because they serve in a broken-down state as the building units from which the animal proteins are made, the latter being the chief organic components of the protoplasm which fills all animal

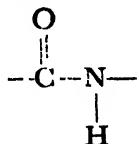
cells. When one speaks of proteins he is therefore getting very close to life itself, and this accounts for the name of these substances, from the Greek word "proteios," meaning primary.

Composition of Proteins. Chemically the proteins are giant organic molecules which contain nitrogen, and perhaps sulfur, phosphorus, and other elements, in addition to carbon, hydrogen, and oxygen. Formulas have been determined for some proteins, by careful analytical work. For example, gliadin, a protein found in wheat, has been given the formula $C_{685}H_{1083}N_{196}O_{211}S_6$. Hemoglobin, the red coloring matter in blood corpuscles, is probably $C_{2962}H_{4664}O_{832}N_{812}S_8Fe_4$. No structure has ever been certainly worked out for a complete protein molecule, although these have been proposed for some of the simplest proteins, such as the fibroin found in silk.

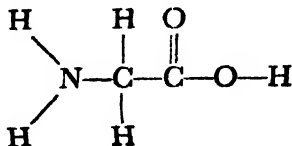


Portion of linear fibroin molecule of silk. Compare with the structure of nylon (page 483).

A significant part of the molecular structure of proteins appears to be the *peptide* linkage, shown below.



This linkage apparently comes about as proteins are built in living plants and animals by the splitting out of water from molecules of *amino acids*. The latter are organic compounds containing carboxyl ($-\text{COOH}$) and amino ($-\text{NH}_2$) groups. The simplest amino acid is glycine, or amino acetic acid.



If water molecules can be made to split out in a reaction between the —NH_2 group of one molecule and the —COOH group of another, peptide linkages are formed.

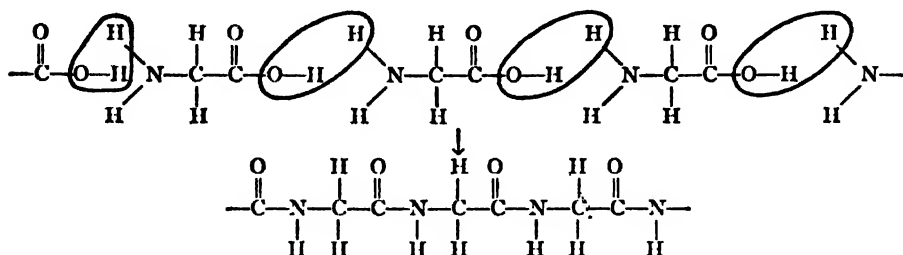


FIGURE 17.5. Formation of Peptide Linkages.

A reaction something like this apparently goes on in living cells in the formation of proteins. However, the splitting out of water cannot be made to take place in such a simple manner in the laboratory. Only by temporarily changing some of the active amino groups to less active derivatives (masking) and making other changes can condensations of amino acids be brought about to yield di- and tripeptides (molecules containing two or three peptide linkages).

Protein molecules have various shapes. Those used as structural building units tend to be long in one direction, like the theoretical product from glycine described above. Actomyocin of the muscles and fibroin of silk are of this type. Those whose function is to act individually in fluids such as blood or milk often have a shape which is roughly spherical. The albumins and globulins are examples of these. At least 30 different amino acids go into the building of proteins, with many types being represented in a given protein; the number of proteins which can exist is therefore seen to be very large.

Some amino acids appear to be essential for normal growth, while others are apparently not needed in the diet. The essential amino acids are given in Table 17.1.

Some Important Proteins and Protein Classes. Fibroin, hemoglobin, and gliadin have already been mentioned. *Casein*

TABLE 17.1 Essential Amino Acids

ARGININE	$\text{NH}_2\text{C}(=\text{NH})\text{NH}(\text{CH}_2)_3\text{CH}(\text{NH}_2)\text{COOH}$
HISTIDINE	$ \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \quad \quad \text{NH} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CCH}_2\text{CH}(\text{NH}_2)\text{COOH} \end{array} $
ISOLEUCINE	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{COOH}$
LEUCINE	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}$
LYSINE	$\text{NH}_2(\text{CH}_2)_4\text{CH}(\text{NH}_2)\text{COOH}$
METHIONINE	$\text{CH}_3\text{S}(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{COOH}$
PHENYLALANINE	$ \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \quad \quad \text{CCH}_2\text{CH}(\text{NH}_2)\text{COOH} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{array} $
THREONINE	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}$
TRYPTOPHAN	$ \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \quad \quad \text{C} \quad \text{CCH}_2\text{CH}(\text{NH}_2)\text{COOH} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{CH} \quad \quad \text{C} \quad \quad \text{CH} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{CH} \quad \quad \text{NH} \end{array} $
VALINE	$(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{COOH}$

is the protein of milk and milk products like cheese. *Keratin* is a fibrous protein found in hair, feathers, hoofs, and claws of animals (also fingernails and toenails of man). *Albumins* are water soluble proteins occurring in such fluids as blood, milk, and egg white. *Collagen* is the chief bone and cartilage protein. It hydrolyzes to the water soluble substance *gelatin*. The *nucleoproteins* are products found in cell nuclei; some virus proteins are also of this type. They contain phosphorus. The *globulins* are water insoluble proteins which, however, dissolve in salt solutions. Serum globulin of the blood is an example.

Self Study Questions

1. What type of organic compound is a fat? What alcohol goes into the formation of all fats and fatty oils?

2. In what way are the acids which are used in fat and fatty oil formation alike? How do they differ? Give examples of a saturated and unsaturated acid obtained from fats.

3. Write the structural formula for glyceryl acetate. Does it occur in fats and oils?

4. What determines the melting point of a fat? How does temperature of formation in living cells appear to affect the composition of a fat?

5. What is meant by hydrogenation of a fatty oil? What change in properties accompanies hydrogenation? What oils are commonly hydrogenated?

6. Assuming 85 per cent efficiency, what volume of hydrogen gas (standard conditions) will be required for the hydrogenation of 1000 grams of glyceryl oleate? *Answer: 89 liters.*

7. What is the etymology of the word "protein"? Why is this name used?

8. What element besides carbon, hydrogen, and oxygen is always present in protein molecules? What additional elements may be present?

9. Write the formulas of possible dipeptides which could theoretically be formed in reactions between lysine and valine?

10. Give examples of some well known proteins.

PART SEVEN

The Chemistry of Living Things

XVIII

Colloid Chemistry

Colloidal Systems. The study of nature would indeed be simpler if molecules were the only aggregates present in the universe (except that the aggregates known as human beings would then not be here to study it). As it is, many aggregates larger than molecules are also apparent, ranging in size all the way from galaxies of stars down to particles consisting of relatively few molecules. The smallest type of these aggregates, often consisting of from a few to a few hundred molecules, is commonly encountered in the study of living things (viruses, for example) as well as in many inanimate systems, organic and inorganic, e.g., a particle of dye, or of clay. The branch of science which deals with these aggregates and the properties peculiar to them is known as *colloid chemistry*. A brief discussion of colloid chemistry is included at this point largely because a knowledge of its principles is helpful in understanding many of the phenomena exhibited by living organisms.

A system containing aggregates of atoms or molecules which fall in the colloidal range (see below) is known as a *colloidal system*, often called simply a colloid for brevity. The individual aggregates are known as colloidal particles, as for example a fog droplet consisting of several hundred water molecules. A colloidal particle need not always be an aggregate, however. In the case of many of our giant molecules, such as those making up proteins, synthetic resins, cellulose, etc., the single molecule may be so large that it falls into the colloidal range of size. Colloidal systems in general consist of more than merely large

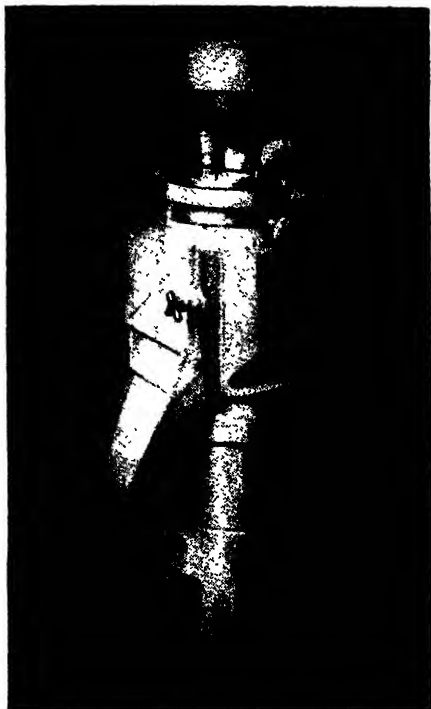
numbers of colloidal particles, since the latter are usually suspended in another medium, as fog droplets in air, gelatin particles or soap particles in water, etc. These systems therefore resemble solutions (page 168), except that colloidal particles have taken the place of the ions or molecules of solute.

Classification of Colloidal Systems. It is an oversimplification to consider colloidal systems as merely colloidal particles suspended in some sort of dispersion medium. However, the particles and the dispersion medium are generally the chief components present, and if other substances are neglected, it is possible to classify these systems according to whether the two phases are solid, liquid, or gas. In Table 18.1 are given some important colloidal systems according to this classification.

TABLE 18.1 Some Important Classes of Colloidal Systems

<i>Class</i>	<i>Name</i>
Solid particles dispersed in a gas	Smoke, fume, haze
Liquid particles dispersed in a gas	Fog
Solid particles dispersed in a liquid	Sol (if fluid), gel (if a jelly)
Liquid droplets dispersed in another, immiscible liquid	Emulsion
Gas bubbles dispersed in a liquid	Froth, foam

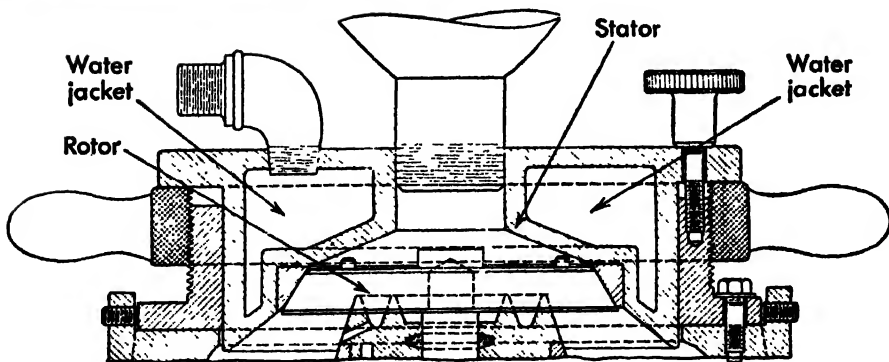
Size of Colloidal Particles. The optical, electrical, and surface properties which distinguish the colloidal state are most pronounced in particles which are below microscopic visibility, and the colloidal size range is therefore assumed by most authorities to lie between molecular and microscopic. If the particles are assumed to be spheres this means they will have diameters between about 5 and 200 millimicrons (page 13). Colloidal properties, furthermore, may also be exhibited by particles colloidal in only two dimensions (filaments, like muscle fibrils), or even in but one dimension (films, like a soap bubble), and the



(a)

subject has been described (Bancroft) as the study of drops, bubbles, grains, films, and filaments.

Preparation of Colloidal Systems. The dispersed phase in colloidal systems is made either by breaking up larger pieces or aggregates of matter (dispersion methods) or by building up colloidal particles from smaller units, as atoms or molecules (condensation methods). An example of a dispersion method is seen in the making of protective coatings, where pigment aggregates are broken up in various ways (page 495) to smaller



(b)

FIGURE 18.1. Colloids by Dispersion. (a) A colloid mill Pastes or liquid suspensions put in at the top are acted upon by strong hydraulic shearing forces as they pass through the region of small clearance between rotor and stator, shown in (b). Courtesy Premier Mill Corporation.

aggregates or particles, at least some of which are in the colloidal range. The making of homogenized milk is another example of

this method of colloid formation. Here the butter fat is dispersed into such small particles that the resulting colloid is more stable than ordinary milk.

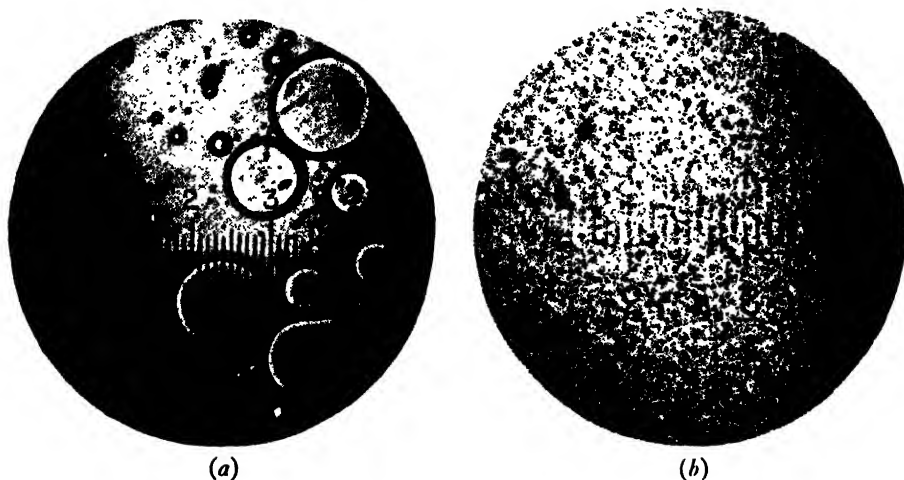


FIGURE 18.2. Oil in Water Emulsions. (a) Before passage through colloid mill, (b) after dispersion by colloid mill. Magnification 250 times. Courtesy Premier Mill Corporation.

An example of a condensation method of preparing a colloid is in the cooling of a hot soap solution, during which soap molecules and ions take on water and come together to produce particles of colloidal size. Many colloidal particles in living organisms are also prepared from smaller units, as proteins from amino acids and starches from glucose.

Adsorption. An important characteristic of colloidal systems is the large total surface of the colloidal particles present. If a cube of substance a centimeter on a side, and having a surface of six square centimeters, is subdivided into smaller cubes each of which is 10 millimicrons on a side, the total surface of these colloidal particles has become six million square centimeters, or about one seventh of an acre. In colloidal systems ions, molecules, and even other colloidal particles are often attracted to this large surface, in a process known as *adsorption*. Examples of this process are the adsorption of toxic gases by the charcoal in a gas mask

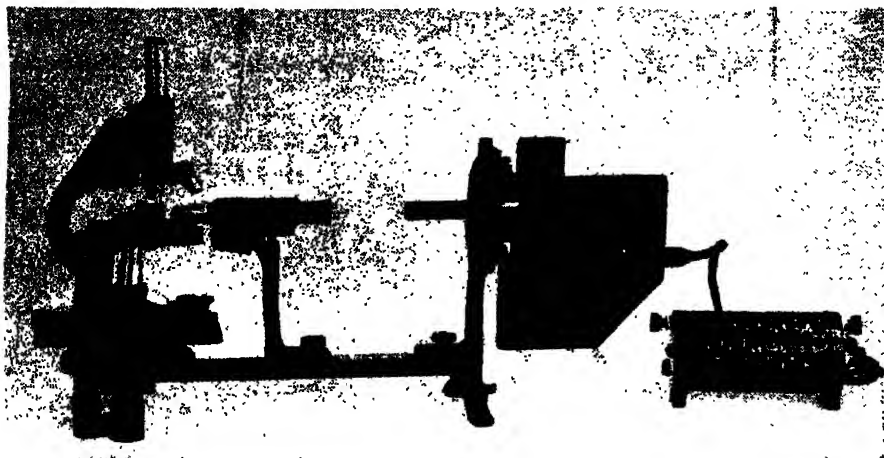
and the adsorption of impurities from lubricating oil when the latter is treated with clay or other inorganic earths during manufacture.

If all of the colloidal particles in a given system adsorb ions of like charge, such as hydroxide ions, the particles become similarly charged, negative in this case. The same effect may also be produced by the ionization of a giant molecule in the colloidal size range. Such systems, with similarly charged particles, are more stable than in the absence of such a charge, because the particles repel each other and therefore do not clump together and form aggregates which rapidly settle out. Most stable colloidal systems have particles which are charged.

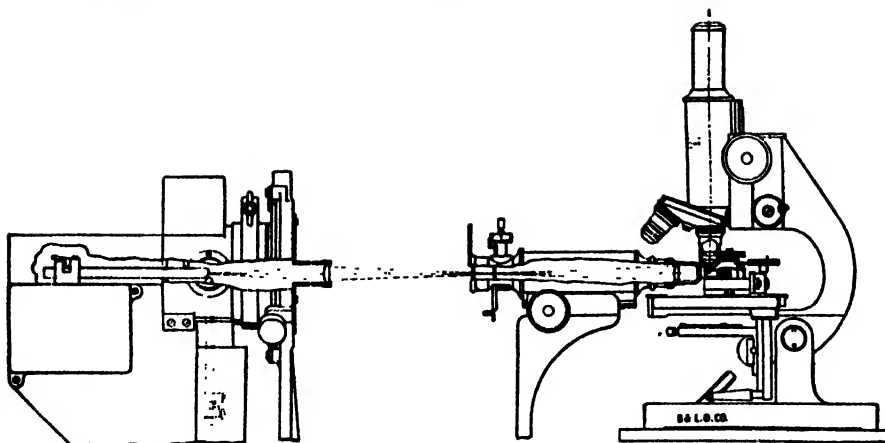
Some colloidal particles tend to adsorb water, causing an increase in particle size, and a higher viscosity, or even a gelling, of the system. Such particles are known as *hydrophilic* (water loving). Gelatin is an example, as are most of the colloids found in living things. Other particles have little affinity for water, and are known as *hydrophobic* (water hating). Colloidal gold suspended in water is in this category.

Brownian Movement. When colloidal systems are examined in a microscope against a dark background, using strong light from the side (dark field illumination), the light is seen to be partially scattered by individual colloidal particles. Part of this reaches the eye and enables the viewer to locate particles, from the observed points of light, which would not be visible in an ordinary microscopic examination, even with high magnification. The instrument which employs this combination of the microscope and the Tyndall effect (page 404) is known as an *ultramicroscope* (Figure 18.3). Particles a few millimicrons in diameter can be located in this manner, as contrasted with the limit of resolution of about 200 millimicrons for a microscope with bright field illumination.

A colloidal system examined in this way in the ultramicroscope presents a striking picture, particularly in the case of small particles in a system of low viscosity, because they are seen



(a)



(b)

FIGURE 18.3. The Ultramicroscope. (a) Colloidal particles in the cell on the microscope stage are made visible by a powerful beam of light from the arc lamp at the right. (b) Light path in this instrument. Courtesy Bausch & Lomb Optical Company.

to be in violent motion, as shown by the rapid, random movements of the many points of light. This motion, already mentioned and explained (page 46) is known as the *Brownian movement*. It is probably our most direct evidence of the still more violent movements of molecules which is postulated by the kinetic molecular theory.

The Brownian movement explains why colloidal particles can diffuse from place to place just as gas or liquid molecules diffuse, and indeed, colloidal particles can be regarded, as far as their kinetic energy is concerned, as simply extra large molecules. Thus it is possible, knowing the mass of a colloidal particle, to calculate what its average velocity must be during Brownian movements, since its average kinetic energy, $1/2mv^2$, will be the same as the average kinetic energy of the molecules of the medium in which it is dispersed.

Settling. If a colloidal particle is denser than the medium in which it is suspended it settles, and if lighter it rises. However, the rate at which these movements take place becomes slower and slower as the size of the particle diminishes. This is illustrated by the data in Table 18.2 for silver spheres in water. A

TABLE 18.2 Rate of Settling of Silver Spheres in Water

	<i>Radius of sphere</i>	<i>Rate of fall in water, centi- meters per second</i>
	1.0 cm.	200,000
	0.1	2,000
	0.01	20
	0.001	0.2
	0.0001	0.002
COLLOIDAL RANGE {	0.00005	0.0002
	0.00001	0.00002
	0.000001	0.0000002

particle in the colloidal range is seen to fall so slowly that very tiny movements in the liquid, produced by earth vibrations or by the convection currents which accompany temperature changes, tend to overcome sedimentation. In a system containing many charged particles, furthermore, settling is also opposed by the repelling effect of particles upon each other caused by their kinetic energy and like charge. Because of these and other factors, many colloidal systems can exist indefinitely without the settling out of particles.

The reason for the slowing up of the rising or falling process as the particles become small is because a greater friction is

developed per unit mass in the case of the small particles. The friction accompanying movement is a function of the surface, whereas the gravitational force producing movement is a function of the mass and the surface-to-mass ratio becomes greater as the particles become smaller. This is entirely different than in a vacuum, where falling is frictionless, causing the rate to be independent of particle size.

The difference in rate of rising or settling is apparent in many colloidal systems in the home. Thus, the tiny air bubbles sometimes seen in freshly drawn, warm tap water rise to the surface much more slowly than coarse bubbles blown with a drinking straw. The butter fat particles in milk which largely constitute cream rise faster in ordinary milk than those in homogenized milk, because they are bigger. A suspension of sand in water settles much more rapidly than a clay suspension, on account of the difference in particle size.

When the charge on colloidal particles is lost, there is a coming together of neutral particles which were previously held apart by their like charges, i.e., the attractive force which exists between all bodies of matter now comes into play, and aggregates are formed from several or many colloidal particles. These settle out of suspension, as explained above, because of their greater mass. When it is desired to bring about the precipitation of colloidal particles, then, the common practice is to neutralize their charge. An example of this is in the elimination of smoke (a colloidal system) from the air by bringing about its precipitation in the chimney or stack where it is rising. The charge is removed electrically, and the smoke particles aggregate and precipitate. Figure 18.4 shows an illustration of this.

Another example of the same general process is the thunderstorm. Many small, charged water droplets may form in a cloud. The charge is suddenly removed as lightning, following which there is a rapid coming together of small droplets to form large, quickly falling ones, and a shower results. The first drops of the shower may be unusually large, since they fall more rapidly and reach the earth first. Still other illustrations are in the deposition



FIGURE 18.4. Smoke Abatement. (a) Carbon smoke with precipitator off. (b) Plant still in operation, but smoke precipitator turned on. Courtesy Western Precipitation Corporation.

of soil particles and rubber latex particles. Colloidal soil or clay particles carried to the ocean by rivers settle and form deltas, partly by the slowing up of the current, but also partly because of the loss of charge upon contact with salt water. A negatively charged clay particle, for example, will lose its charge by adsorption of positively charged sodium ions. When a colloidal latex suspension is electrolyzed, negative latex particles are attracted to the positive electrode where they remain, after loss of charge, and the deposited layer takes the shape of the electrode. This is one way in which latex rubber articles are made.

Optical Properties. Colloidal systems often behave in a unique manner toward light, in that they permit passage of part of it (transmitted light) and scatter part of it. If a beam of light is passed through a colloidal system the scattered portion makes the beam visible from the side. This is known as the Tyndall effect, after the British natural philosopher who referred to it often in writings and lectures during the third quarter of the

last century. It is used as a simple test for the colloidal state. (See Figure 18.5.)

The scattered portion often contains most of the short wave length light, and the transmitted portion most of the longer

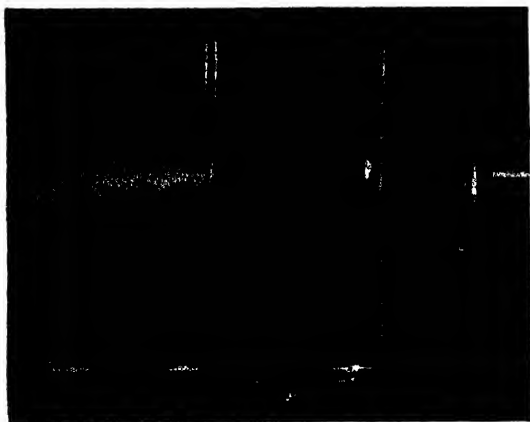


FIGURE 18.5. The Tyndall Effect. An optical characteristic of colloidal suspensions is that they scatter part of a beam of light sideways. The light beam from lamp L is being passed through pure water W and a colloidal suspension of soap in water S. From Black and Conant, *New Practical Chemistry*, Revised Edition, Copyright, 1942, by The Macmillan Company.

wave lengths, when polychromatic incident light is employed. When sunlight passes through a suspension of clay and water, for example, the scattered light is bluish and the transmitted light reddish in appearance. Several optical phenomena in nature can be explained on this basis, and red sunsets and blue skies are merely examples of the Tyndall effect on a giant scale, produced by colloidal material in the atmosphere (page 93). Twi-

light, also, is produced by scattered sunlight after the sun has set, the light being turned downward after it hits colloidal material high enough in the air to be still in sunlight. This period lasts much longer in northern regions because the sun, setting obliquely, remains only a short distance below the horizon for some time.

Semipermeable Membranes. When a complex colloidal system consisting of colloidal particles, molecules of dispersion medium, and various other ions and molecules, is poured into a container with porous walls which permits everything but the colloidal particles to pass through (a *semipermeable* container, or one having a semipermeable bottom made of, say, parchment

or cellulose nitrate), several things may happen. In the simplest case the various ions and molecules will filter through and leave the colloidal particles behind (ultrafiltration). Or, the semipermeable container may be immersed in the pure dispersion medium, whereupon ionic and molecular impurities diffuse out, and the colloidal system becomes purer (dialysis) (Figure 18.6).

Dialysis is complicated in many cases by electrical charges, as well as by adsorption and solubility phenomena in connection with the membrane, making this a difficult subject in which to predict results beforehand. However, colloidal behaviour toward semipermeable membranes is of the greatest importance in the chemistry of living organisms, since the

latter consist very largely of these membranes, as in lungs, blood vessels, intestinal walls and cell walls in general. For example, in the kidney glomerulus, a semipermeable membrane filters non-colloidal solutes and water from the highly colloidal blood plasma. Further along in the same process water, glucose, amino acids, and other molecules are reabsorbed through another membrane before the residual liquid, urine, is formed. One of the key research problems in biochemistry is that of learning about the complex colloidal processes which occur in connection with the semipermeable membranes in living organisms.

Protection. When hydrophobic and hydrophilic colloidal systems are mixed several changes may occur. A common phenomenon is the coating of the hydrophobic particles with the hy-

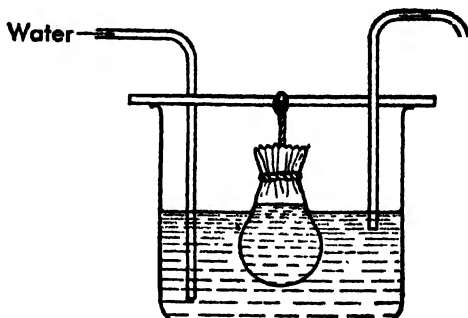


FIGURE 18.6. Apparatus for Dialysis. The sack, which might be made of cellophane, pyroxylin or parchment, is a semipermeable membrane which permits diffusion of ionic and molecular impurities into the flowing water, but retains the colloidal particles. From Sisler, Vander Werf and Davidson, *General Chemistry; A Systematic Approach*. Copyright, 1949, by The Macmillan Company.

drophilic ones, or at least a process which yields results similar to those expected if a coating had taken place, since the mixture now takes on the properties of a hydrophilic system. Thus,

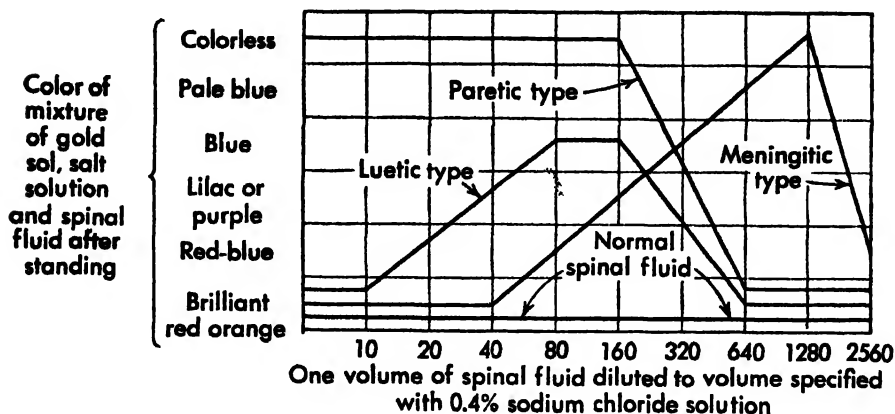


FIGURE 18.7. Difference in Behaviour of Normal and Pathological Spinal Fluid toward Gold Sol. Normal spinal fluid has a high protective effect at all dilutions shown. The pathological fluids show poor protection at characteristic dilutions.

colloidal gold suspended in water is a typical hydrophobic system, low in viscosity and easily precipitated by small amounts of electrolytes, whereas a gelatin suspension in water is as typically hydrophilic, with high viscosity and low sensitivity to electrolytes. Now if the two are mixed, the resulting system is still hydrophilic, and the gold sol has been made much more stable. This process is called *protection*, and the gold sol is said to be protected by the addition of gelatin.

Two applications of protection will be mentioned. One is the stabilization of a number of hydrophobic systems of commercial importance, such as Argyrol (colloidal silver), and India ink (colloidal carbon), by addition of hydrophilic colloids. The other application makes use of the hydrophilic nature of body fluids, and their change in protective ability under pathological conditions. For example, the spinal fluid of a healthy individual has a high protective action on colloidal gold, whereas in some types of disease the protective ability drops. This can be experimentally determined, and thus furnishes a method of diagnosis,

particularly since different types of disease give a different protection curve with progressive dilution of spinal fluid, as shown in the graph in Figure 18.7.

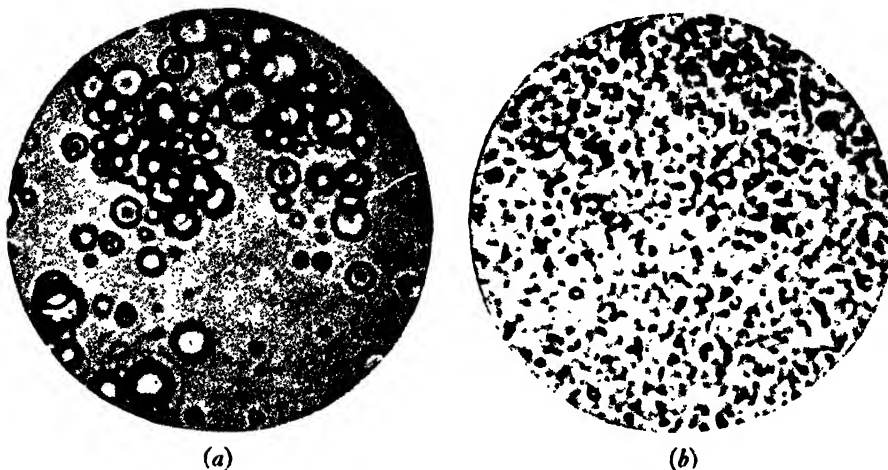


FIGURE 18.8. Milk, Magnified 2250 Times. (a) Normal pasteurized cow's milk without homogenization, (b) pasteurized cow's milk, homogenized. (Courtesy National Dairy Research Laboratories, Inc.)

Colloidal Systems in the Home. *Milk*, a dispersion of butter fat in a water solution of milk sugar, proteins, and salts, has already been mentioned. The *butter* obtained by churning milk is itself a colloid, containing as dispersed substances salt water and air. Many other food substances are also colloidal, including water suspensions of *gelatin*, *starch*, and the more complex products made by cooking *cereals* with water. *Mayonnaise* is an emulsion of vegetable oil in dilute vinegar solution, stabilized by substances present in egg yolks. Other stabilizing agents may be used, particularly in products known as "salad dressing." *Cold cream* is chiefly an emulsion of water droplets in mineral oil. *Vanishing cream* is mainly a suspension of stearic acid in a water solution of soap and glycerine. *Paints* can be considered as colloidal suspensions of pigment in oil, although the particle size of such pigments is often larger than the colloidal range. *Enamels*, *lacquers*, and *varnishes* contain in addition natural or synthetic resins, the particles of which are of colloidal size. Water solutions

of *soap* and other detergents are generally colloidal systems, due to formation of aggregates by association of groups of detergent molecules or ions. When these clean they also cause the removed dirt to form a colloidal suspension in the detergent solution. The foam associated with detergent solutions, as well as that which forms on some beverages, is also colloidal in nature, since the bubble walls are films sufficiently thin to exhibit colloidal properties.

Self Study Questions

1. Name several classes of colloidal systems based upon the states of matter. Give examples.

2. In what size range do most colloidal particles fall? Are colloidal properties exhibited only by particles colloidal in three dimensions? Explain.

3. Give examples in which adsorption of substances on large surfaces serves a useful purpose.

4. Distinguish between hydrophilic and hydrophobic colloidal particles. Give examples of each.

5. How can the Brownian movement of a colloidal particle be observed? What is the explanation for this movement?

6. Explain why a small gas bubble rises more slowly from a suspension than a large bubble of the same gas.

7. Why does loss of charge by colloidal particles result in their settling out? Give examples of this process.

8. What is the Tyndall effect? How does the average wave length of the scattered light under these conditions compare with that of the transmitted light? Give examples of the Tyndall effect in nature.

9. Define dialysis, ultrafiltration, semipermeable membrane. Give examples in nature of the operation of semipermeable membranes.

10. What is meant by the term "protection" in colloid chemistry? Give applications of this phenomenon.

11. Describe several colloidal systems found in the home.

XIX

Plant Chemistry

The chemistry of living things (biochemistry), is so complicated that the utmost is required in human intelligence and in experimental ingenuity before we can begin to understand it. Most biochemists would probably agree that only a start has been made in learning of the chemical changes which occur in plants and animals. In spite of the complexity of biochemistry, human beings are probably more interested in learning something of the chemical changes which take place in their own bodies and in the growing plants around them than they are in any other chemical topic; a brief discussion of biochemistry accordingly belongs in a book such as this one.

Plant chemistry is slightly less complicated than that involved in the life processes of animals because most plants make their substance, as they grow, out of relatively simple chemicals found in the air and in water solutions. Animals, on the other hand, live on already formed and very complicated plant and animal material. Plant chemistry belongs first, therefore, in a study of the chemistry of living things.

It should be kept in mind that our knowledge of the chemical changes in plants (and animals) is fragmentary, and exceedingly difficult to gain, because of a serious experimental limitation. The chemical balance in a plant is so delicate that many of the experiments we would like to try cannot be performed because they kill the plant, or injure it to the point where the chemical change being studied fails to take place, or the chemical substances being sought are destroyed in the experiment. Bio-

chemistry is therefore still very much in the hypothesis stage, accounting for the rather frequent use of such expressions "as it is thought to be" or "it appears likely."

FORMATION OF PLANT SUGAR

The Chemical Intake. Plants, and all other living things, grow by the formation of many different kinds of *cells*. The microscopic structure, reproduction, and other properties of these constitutes the fundamental base of the science of biology. Chemically these cells are chiefly water containing a highly complex mixture of proteins, carbohydrates, fats, pigments, inorganic ions, and other substances. As the plant grows, i.e., as it makes new cells, it must take up additional supplies of chemicals to form these. It does this in two ways. Carbon dioxide diffuses in through tiny openings in the leaves (stomates). Water and soluble salts enter through the roots, supplying the necessary elements hydrogen, oxygen, nitrogen, sulfur, phosphorus, potassium, calcium, magnesium, and traces of iron, copper, manganese, zinc, boron, molybdenum, and probably others.

The Coming Together of Assimilated Substances. The first important chemical change between the substances taken in by plants is thought to be that involving carbon dioxide and water. But these must be brought together before they can react, since one enters through the leaves and the other through the roots. The two combine in the leaves, hence water must rise from the plant roots prior to the reaction. Several forces aid in causing this ascension of water.

The principal force is probably that due to *osmosis*. To understand osmosis it is necessary to recall that because of their kinetic energy (page 47) water molecules at ordinary temperatures are in constant motion. It is largely this motion which is thought to carry water molecules into the plant roots, the entry perhaps being made through very narrow openings between bundles of cellulose molecules. If the cell walls were simply permeable membranes, with pure water within and without, water mole-

cules would diffuse in and out at the same rate, without the developing of internal pressure except perhaps small effects due to capillary forces. But in the protoplasm within the cell walls are large organic molecules which attract the incoming water molecules. The resulting loosely bound aggregates are too large to pass out from the cell.¹ While some water molecules do escape from these aggregates and pass out, the overall rate at which water leaves is slower than that at which it enters, and an internal pressure is consequently built up which causes a water solution to rise from the roots. Osmosis, then, is *the passing of a liquid through a semipermeable membrane² into a solution in which that liquid is the solvent*. Plants contain tiny tubes (xylem) which are filled with this watery solution which rises largely as the result of osmosis. These tubes are formed from lines of connecting cells with permeable or open ends.

A considerable pressure is built up in this way. For example, a pressure of 90 pounds per square inch has been measured in excised tomato plant roots (sufficient to push a column of water up several hundred feet). However, as more water passes through such a semipermeable membrane the solution formed within becomes more dilute, and a hydrostatic pressure (that due to a difference in water levels) also develops. If these two factors become large enough, water molecules pass out through the cell membranes in the roots as rapidly as they enter, and a state of equilibrium is reached.

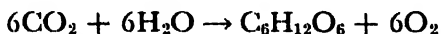
Another force aiding the rise of water in plants is thought to be that due to evaporation of water from plant leaves (transpiration). This dehydrates the cells in the spongy layer of the leaf, and they in turn take more water from neighboring cells, and so on, creating a demand for water at the top of the plant which

¹ An oversimplification, however. This implies that the membrane acts merely as a sieve. Cell membrane permeability is also determined to some extent by surface tension factors, and by the specific nature of the molecule in question. Because of this, membranes are sometimes permeable to large molecules and impermeable to smaller ones. For this reason the biologist prefers to use the expression "differentially permeable" rather than the chemist's word "semipermeable."

² See page 404.

is supplied by that pushed up from below. As the result of these forces water and dispersed salts may be carried to great heights in some plants, as much as 300 or 350 feet in the case of some of the taller trees.

Photosynthesis. When water reaches the leaves from the roots, part of it evaporates, but another part undergoes a remarkable chemical reaction with carbon dioxide—*photosynthesis*—which is directly or indirectly the basis for all life. If the change is expressed merely in terms of the starting chemicals and products, then carbon dioxide and water react to form glucose³ and oxygen.



(674,000 calories of energy absorbed per mol of glucose formed)

However, the reaction does not take place in one step, i.e., there could not in general be a simultaneous coming together of six

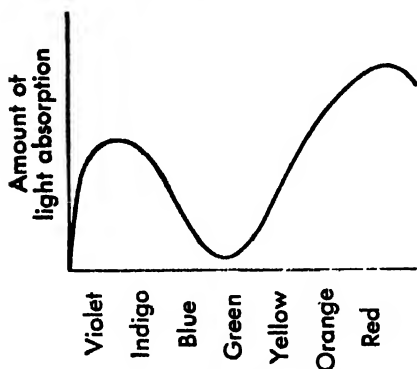


FIGURE 19.1. Light Absorption by Plants.

carbon dioxide molecules and six water molecules, since such a meeting on a large scale would be statistically impossible. One of the great fundamental problems in biology and chemistry is that of determining the intermediate steps which add up to the above reaction, and the catalysts required to bring them about. Much work is being done in attempts to learn these steps.

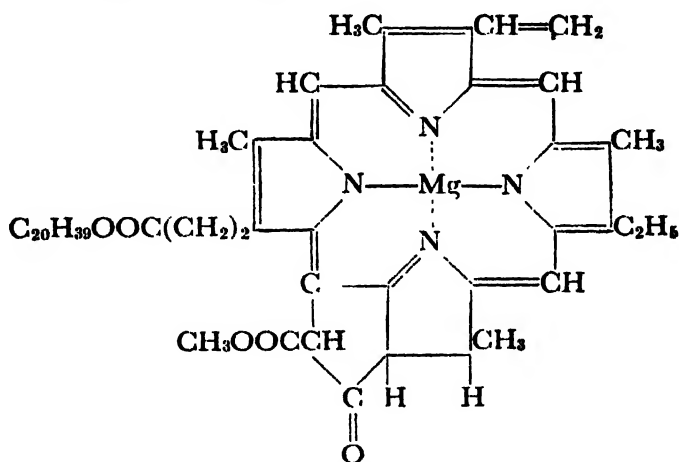
Of particular interest at the present time is research involving use of radioactive isotopes. It has been found by using molecules containing "tagged" atoms, for example, that the evolved oxygen comes from the water and not from the carbon dioxide.

Since photosynthesis is endothermic (page 73), energy must

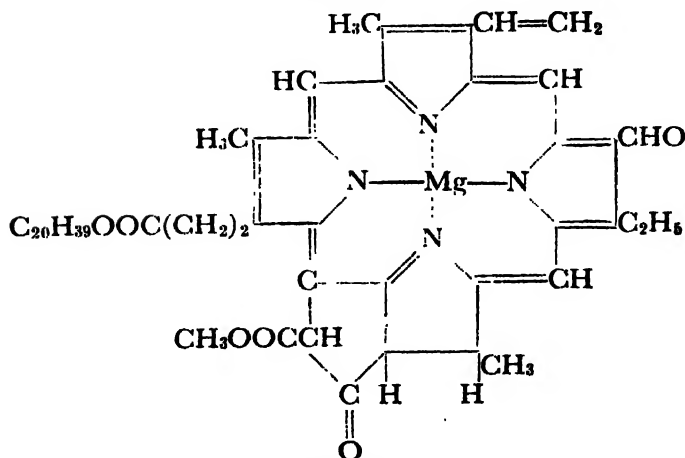
³ Some authorities prefer to say "organic matter" rather than glucose, because while glucose is eventually formed, it may not be the first product of the reaction. In Calvin's photosynthesis cycle, involving ten steps, a hexose (e.g., glucose) is assumed to be formed from 2-phosphoglyceric acid at the second step.

be supplied from without before it will take place. This energy, as the name implies, is absorbed in the form of light (photosynthesis—a building up with the aid of light). The photosynthesis reaction takes place in the presence of radiation in the red (chiefly) and blue regions of the visible spectrum, as shown by the graph in Figure 19:1. Sunlight is of course the main source of this radiation.

There are present in plant cells tiny bodies known as chloroplasts which contain a green substance made up of two very similar molecules, chlorophyll A and B.



Chlorophyll A



Chlorophyll B



FIGURE 19.2. Fumigating Storage Vaults for Plant Products. Methyl bromide fumigant is being used. Courtesy The Dow Chemical Company.

These absorb red and blue light (and reflect green, accounting for their color). The chlorophylls apparently cause a conversion of radiant energy to chemical energy, because the endothermic photosynthesis reaction begins in the region of the chloroplasts, as evidenced by the fact that oxygen has been detected first in these parts of cells. There may be several dozen chloroplasts in a single leaf cell, and such tremendous numbers are present in the whole leaf that the entire surface appears to be green. It seems likely at this time that carbon dioxide and water react and become fixed in some way even in the absence of visible light, in a step known as the dark reaction, but the final conversion to sugar and oxygen then requires the radiant energy supplied by some of the visible portions of sunlight.

OTHER SUBSTANCES FORMED IN PLANTS

The sequence of reactions in plants is not very well known. However, it appears likely that the sugar first formed as the result of photosynthesis serves as a basic material for the building of other types of plant molecules.

Starch. The sugar molecules formed early in the plant's production schedule are able to pass through permeable cell walls and move from cell to cell, in this way spreading from the leaves throughout the plant. This is done chiefly in an arterial network of living cells known as the phloem. Part of the sugar is converted to starch (page 376). The latter seems to constitute a nondiffusible sugar reservoir, from which diffusible sugar can readily be obtained again as needed, according to the reversible equation:



It appears that the glucose or other sugar which forms in leaf cells during periods of photosynthesis is often quickly changed to starch in the leaves, but this then later reconverts to sugar which diffuses throughout the plant. Part of the sugar again changes to starch after the diffusion, often in the roots, where it remains until a time of need, such as during the first growth of a potato plant, for example.

It is interesting to note that animals similarly convert glucose to starch for storage purposes. This is done in the liver, and the product is known as animal starch, or glycogen. Starch also has been found in certain fungi and insects.

Cellulose. At least a third of the glucose generated by plants is changed to cellulose. Molecules of this substance are the building units which make up the rigid structure of plants. Cellulose molecules are thought to form from as many as 10,000 glucose molecules as shown in the equation below.



The values for y are on the average probably somewhat larger than those for x in the starch equation above. There is also a fundamental difference in the way the glucose units are joined together in starch and cellulose (pages 376 and 379).

The reader should keep in mind the relative sizes of things in comparing living cells and molecules. Cellulose has been called a giant among molecules, but living cells are so much

larger than dozens or even hundreds of cellulose molecules can be placed end to end in the distance which is a cell dimension."

The change from glucose to cellulose does not appear to be as easily reversible as that between glucose and starch, and the woody (cellulosic) part of a plant remains long after the death of the cells which originally generated it.



FIGURE 19.3. Plant Examination. The effect of a new insecticide is being studied. Courtesy The Dow Chemical Company.

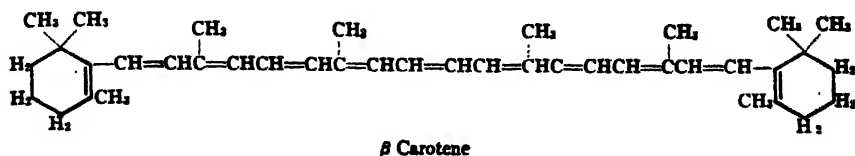
Chlorophyll and Other Colored Plant Substances.

The green substances in leaf cell chloroplasts which apparently have much to do with photosynthesis are the chlorophylls A and B, shown on page 413. A magnesium ion is seen to be the key element in this unusual type of molecule. Magnesium is therefore necessary for a healthy plant, and a trace of iron is also required before the chlorophylls will form, although no iron is present in these molecules. It may be

that iron is the central atom in a prechlorophyll molecule and is later replaced by magnesium. In this connection it is of interest to note the similarity between chlorophyll and the heme part of the red hemoglobin present in the blood of vertebrates (page 439), a difference being that magnesium is the central atom in the former and iron in the latter. Plant and animal chemistries are alike in many respects, and here is an example of two rather similar molecules, each being part of a vital, colored substance.

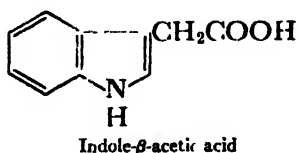
Many other colored molecules are made by plants. Among these are the carotenoids, some 60 of which are known at the

present time. Carotenoids are responsible for the yellow color of carrots, butter, and egg yolks. The formula for β carotene is given below. It is closely related to vitamin A (page 451).



Red substances known as anthocyanins are also formed in plants. These are responsible for the red color seen in autumn leaves, when conditions are not right for further production of chlorophyll. Indigo, litmus, henna, and madder are a few of the many other pigments found in plants. Flowers often have litmus-like colors that can be varied, red or blue, by making them acid or alkaline.

Plant Hormones; Weed Killers. Among the chemical substances formed by living plants are some which appear to regulate certain phases of plant growth or behaviour. These are called *hormones*. They are also known to the biologist as auxins, and by other names.⁴ A few hormones have been isolated, the best known being indole- β -acetic acid.



Synthetic substances such as sodium naphthalene acetate and 2,4-dichlorophenoxyacetic acid also have a hormone-like action on plants. It is not known how many phases of plant life are affected by hormones and related synthetics, but at the present time these compounds are used, in very low concentrations, to speed up root formation in cuttings, to force a crop of plants

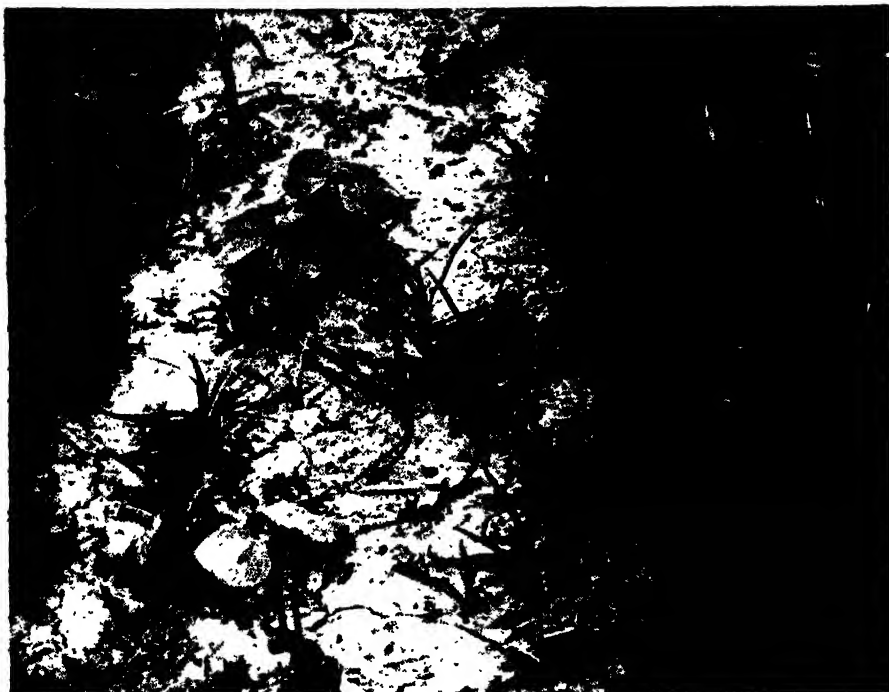


FIGURE 19.4. Weed Control. The band shown, containing cotton plants, was treated with alkanolamine salts of dinitro-*o*-sec-butylphenol, which kills seeds germinating in the top quarter or half inch of soil. Nutgrass is the only weed which survived this treatment. The untreated areas are infested with pigweed and crabgrass. Courtesy The Dow Chemical Co.

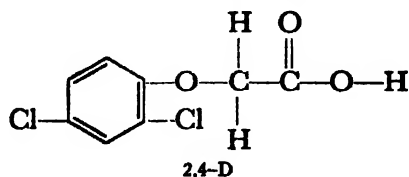
uniformly into flower so that the later harvesting of fruit can be done more efficiently, to prevent premature dropping of fruit from trees, to cause a more rapid ripening of fruit, and even to grow seedless fruit without pollination, since the fleshy part of the fruits of some plants such as melons, tomatoes, or figs will develop upon application of the proper auxin to the pistil of the flower.

The substance 2,4-dichlorophenoxyacetic acid (2,4-D) and the related mono and trichloro compounds have a remarkable variety of effects upon plants. 2,4-D is used at very low concentration to bring about a more rapid ripening of bananas and figs. It likewise inhibits preharvest drop of citrus fruits, and the fruit apparently stores better after treatment with this substance.



FIGURE 19.5. Spraying Hops for Insect Control. Courtesy The Dow Chemical Company.

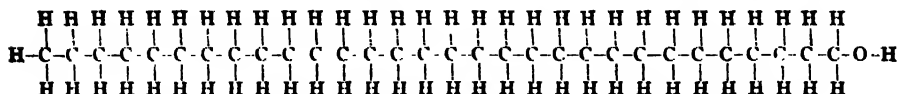
2,4-D is also a powerful weed killer. Employed at the proper concentration on a lawn it kills such broad-leaved weeds as



plantain and dandelions but does not permanently injure the grass. There is some uncertainty as to its action. One theory is that it causes plants which it affects to burn up their food reserves through increased respiration (see below), but this is not accepted by all authorities.

Other Substances Made by Plants. Proteins, described earlier (page 388), are a vital part of plant and animal cells. These cells contain a semifluid mixture, protoplasm, present as cytoplasm and cell nuclei. The chief component of protoplasm is water (70–90 per cent). Next in quantity is protein, followed by carbohydrates, fats, and many other substances. The protein content is about equal to the total of the other solid components of protoplasm. As mentioned earlier, proteins are thought to result from condensation of many amino acid units, with splitting out of water (page 390). Amino acids in turn are believed to be formed when glucose or one of its precursors in the photosynthesis process reacts with nitrogen-containing ions.

Oils, fats, and waxes are products of plant chemistry. Oils and fats have been discussed earlier (page 383). Waxes are related to these in that they too are esters (page 356), but usually of larger molecular weight. The alcohols which go into the formation of wax esters have more carbon atoms than glycerine, and contain but one hydroxyl group. Carnauba wax, for example, obtained from palm leaves, is rich in an ester of myricyl alcohol,



and cerotic acid.

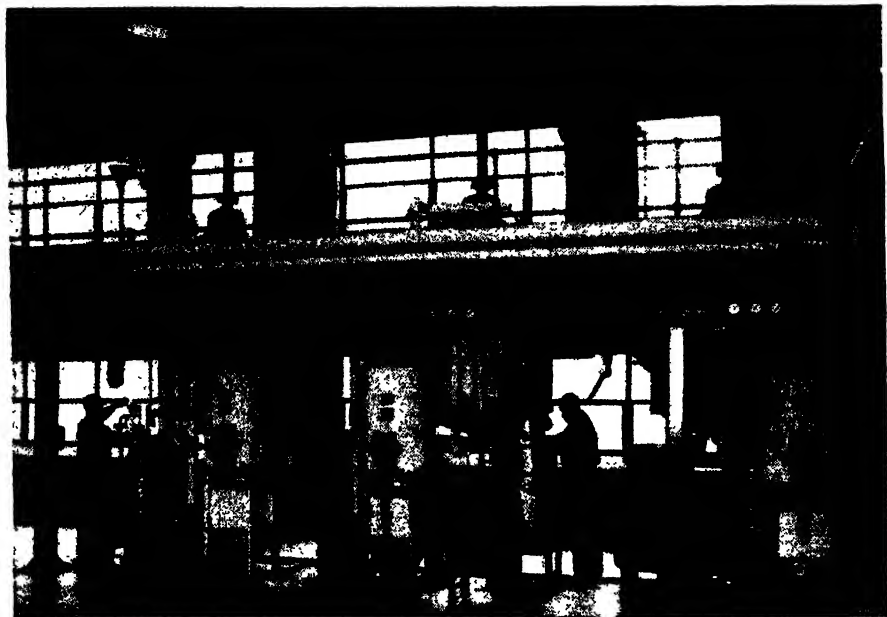


FIGURE 19.6. Steam Distillation of Essential Oils. Oil of ginger is being distilled from ground ginger root in a battery of three stills. Courtesy Fritzsche Brothers, Inc.

Essential oils, not to be confused with the fatty oils mentioned earlier, are formed by most plants. They account for the aromatic and fragrant odors of flowers and other parts of plants. They are thought to aid in attracting insects for pollination purposes. These oils are often terpenes, $C_{10}H_{16}$ (page 345), or their oxygen derivatives. For example, rose oil is largely the substance geraniol, $C_{10}H_{18}O$.

Many other complex chemicals are made by plants, including vitamins, discussed in the next chapter, resins such as the rosin from pine trees, glycosides (combinations of sugars and other substances to form large molecules), and alkaloids (alkaline organic nitrogen compounds, such as strychnine and quinine).

ROLE OF INORGANIC IONS IN PLANTS

The complex nature of plant chemistry can better be realized when some of the functions of the elements present in plants other than carbon, hydrogen, and oxygen are described. The

following elements, present in ions taken in through plant roots, are essential for plant growth.

TABLE 19.1 Necessary Elements Absorbed by Plant Roots in Ion Form*

<i>Element</i>	<i>Absorbed as</i>	<i>Function</i>
NITROGEN	Nitrate or aminonium ion	Needed for formation of plant proteins. Stunting of growth occurs in its absence.
SULFUR	Sulfate ion	Necessary in some proteins and glycosides.
PHOSPHORUS	Phosphate ion	Needed in enzymes and nucleoproteins.
MAGNESIUM	Magnesium ion	Required in chlorophyll.
CALCIUM	Calcium ion	Needed in compounds which affect the permeability of cell walls.
IRON	Iron ions	Required for synthesis of chlorophyll.
POTASSIUM	Potassium ion	Function uncertain. Probably required in enzymatic processes. Only traces of the last four are needed.
MANGANESE	Manganous ion	
COPPER	Cupric ion	
BORON	Borate ion	
ZINC	Zinc ion	

* This list is probably not complete, since further essential trace elements are being reported from time to time. Molybdenum may be needed in traces.

RESPIRATION

All plants (and animals) must have energy to carry on living functions. This energy is largely produced by the oxidation of complex molecules, the process being known as *respiration*. If glucose is so oxidized, for example, the products are carbon dioxide and water. Respiration in animals puts oxygen into the



blood and hence brings about similar exothermic reactions. Plant respiration occurs extensively, for example, during the germination of seeds. It is also thought to take place in plant roots, causing a giving off of carbon dioxide to the soil in the immediate neighborhood of the roots. This in turn is thought to cause an increase in soil acidity, since water is available for the

formation of carbonic acid. The increase in acidity may help to put into solution some of the mineral constituents of the soil necessary for plant growth.

FERTILIZERS

Fertilizers are materials added to the soil to supply essential elements which happen to be depleted in the untreated soil. Nitrogen, phosphorus, and potassium are the major elements most likely to be needed, since they tend to be taken from the soil by growing plants. There is also evidence that soils may become deficient in some of the trace elements. All-purpose fertilizers commonly contain nitrogen, phosphorus, and potassium, and often have calcium and sulfur present also. The percentages of nitrogen, phosphoric acid, and potash⁵ is usually shown by three consecutive numbers marked on the container. Thus, a 4-12-4 fertilizer means one containing the stated percentages of those substances.

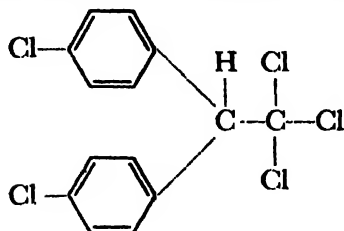
Compounds present in inorganic fertilizers include nitrates of sodium, potassium, calcium and ammonium, ammonium sulfate and phosphate, calcium cyanamide (CaCN_2), calcium acid phosphate (superphosphate of lime, $\text{Ca}(\text{H}_2\text{PO}_4)_2$), calcium sulfate, potassium chloride and carbonate, and others. Organic fertilizers are also widely used, the commonest being manure. Mixtures of organic and inorganic fertilizers, such as manure plus a phosphate fertilizer, are frequently employed, and constitute a very desirable method of soil treatment.

INSECTICIDES

These are substances that kill the insect pests which attack plants. In the past inorganic compounds of arsenic, lead, copper, and fluorine were generally used for this purpose, together with a few naturally-occurring organic compounds, such as nicotine, pyrethrum, and rotenone. In recent years a number of additional organic compounds have been synthesized which are far more

⁵ Potassium carbonate.

deadly to insects than the earlier types. The substance DDT (dichlorodiphenyltrichloroethane) is the best known of these. It is effective in low concentration against such pests as the Japanese beetle, the gypsy moth,



corn borers, and cotton bollworms. It also has the advantage that it is relatively nonvolatile, and an area may be protected for months following an application. Since the advent of DDT many other organic chlorine, sulfur, and phosphorus compounds have been found to be effective insecticides.



FIGURE 19.7. Preparation of Radioactive Insecticide. Absorption of insecticide by plant can be checked by tracer methods. Protective coat is being worn to avoid radiation injury. Courtesy The Dow Chemical Company.

SOILLESS GROWTH OF PLANTS

The function of soil during plant growth is to anchor the roots and to provide water and the essential inorganic ions. These functions can also be fulfilled without the use of soil, and healthy plants can be grown whose roots merely dip into a water solution containing the necessary ions. This interesting method of growing plants has been called hydroponics, or soilless growth of plants. It is becoming of commercial importance.

Many chemical mixtures have been suggested for use in hydroponics, such as one consisting of calcium nitrate, potassium nitrate, potassium acid phosphate, and magnesium sulfate. The trace elements described above must also be present, and small

amounts of a separate solution containing these are added from time to time. The acidity of the solution which bathes the roots is of great importance in determining the success of the process.

Two mechanical problems which arise in hydroponics are holding the roots firmly enough to anchor the plant and aerating them. Excelsior, sand, gravel, or cinders can be used for holding the roots in place. Aeration is provided either by bubbling air through the solution or by lowering the latter from time to time so that air can get to the roots.

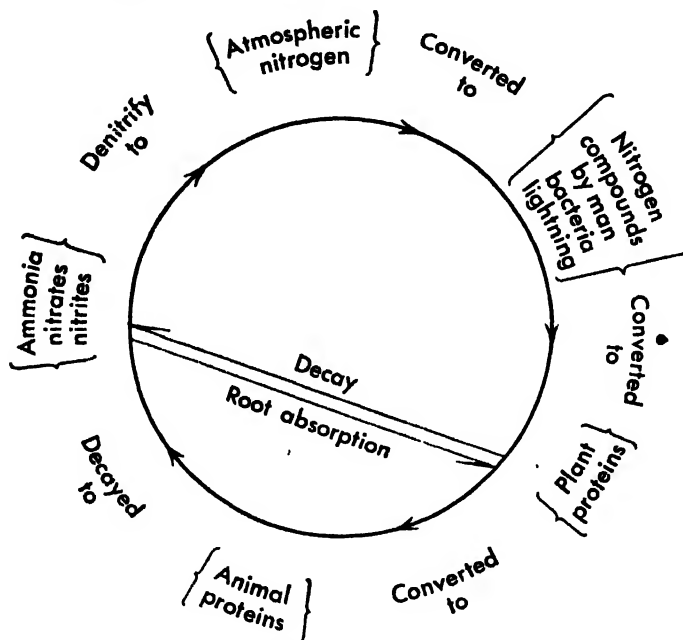


FIGURE 19.8. The Nitrogen Cycle.

CHEMISTRY OF PLANT DECAY

Dead plant matter, particularly in the presence of soil and water, undergoes a chemical disintegration which eventually leads to the reformation of simple inorganic molecules. The process is brought about by a number of different fungi and bacteria. Some of the latter thrive in the presence of air (aerobic), while others are active only in its absence (anaerobic). As the result of this attack the cellulose of a plant is slowly converted to

carbon dioxide and water, the protein nitrogen to ammonia, nitrites or nitrates, the sulfur to hydrogen sulfide or higher-valenced sulfur compounds, etc. The plant structure shrinks and eventually disappears, releasing chemicals which again become available to living, growing plants. The partially disintegrated material makes up the dark-colored portion of soil known as humus. The chemical cycle involved in growth and decay can be illustrated with nitrogen, as shown in Figure 19.8. Each of the other elements needed by plants has its own cycle.

Self Study Questions

1. What are the points of entrance of chemical substances in plants? What essential elements are taken in at these points? How would you proceed, experimentally, to determine whether an element¹ was essential for plant growth or not?
2. What forces are thought to cause water to rise from plant roots to the leaves? What is osmosis?
3. Write an equation representing the overall chemical change in photosynthesis. Why could this reaction not proceed, on a large scale, in one step?
4. Why does not photosynthesis take place when carbonated water is exposed to sunlight?
5. Illustrate with an equation the formation of (a) starch, (b) cellulose, from glucose as we think it takes place in the plant. Which of these reactions is the more reversible under the conditions existing in the plant? What is the evidence on this point?
6. Describe roughly the difference in size between a cellulose molecule and a plant cell.
7. What is the function of chlorophyll in the plant? Account for its green color in terms of light absorption. What similar molecule is present in the human body? What are the metal ion components of these two molecules?
8. Calculate the calories of energy necessary to form a pound of glucose from carbon dioxide and water by photosynthesis.
9. What are plant hormones? Give an example of a synthetic chemical which exerts a hormone-like action on plants.

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10. How are proteins believed to be synthesized in plants? Oils, fats, and waxes? Give examples of other substances formed in growing plants.

11. What elements are commonly supplied to the soil by use of fertilizers? In what form are these elements present in fertilizers? What is meant by a 4-12-4 fertilizer?

12. Describe how it is possible to grow plants without the use of soil. Suggest a group of electrolytes, which will supply essential elements, which is different from the mixture given in the book.

13. Discuss briefly the chemistry of plant decay.

XX

Chemistry of the Human Body

This, the main field of biochemistry, has expanded rapidly in recent years, largely as the result of the application of new fundamental techniques to biochemical research, and the science has now grown to a very considerable body of knowledge. However, biochemists in general would probably agree that in spite of all we now know, only a start has been made in understanding the whole chemistry of the living body, so great is its complexity. The brief discussion of human biochemistry which follows will first deal with the digestion of food, its use and the elimination of its end products. The chemistry of blood, lymph, bone, and muscle will then be considered, followed by a discussion of classes of chemical substances of importance to life, such as enzymes, hormones, vitamins, chemotherapeutic agents, etc.

DIGESTION

Nature of Digestion. The food which human beings consume is composed in part of substances assimilated by the body and in part of substances not assimilated which pass on through the alimentary canal. The processes which occur during the taking up of the portion used by the body go under the general heading of *digestion*. The substances assimilated are chiefly water, mineral salts, carbohydrates, fats, and proteins. Most of the molecules of the last three classes of substances are too large to pass through the intestinal walls, and they are absorbed only after they have been broken down into smaller units in a series of reactions which are catalyzed by chemicals supplied by the body

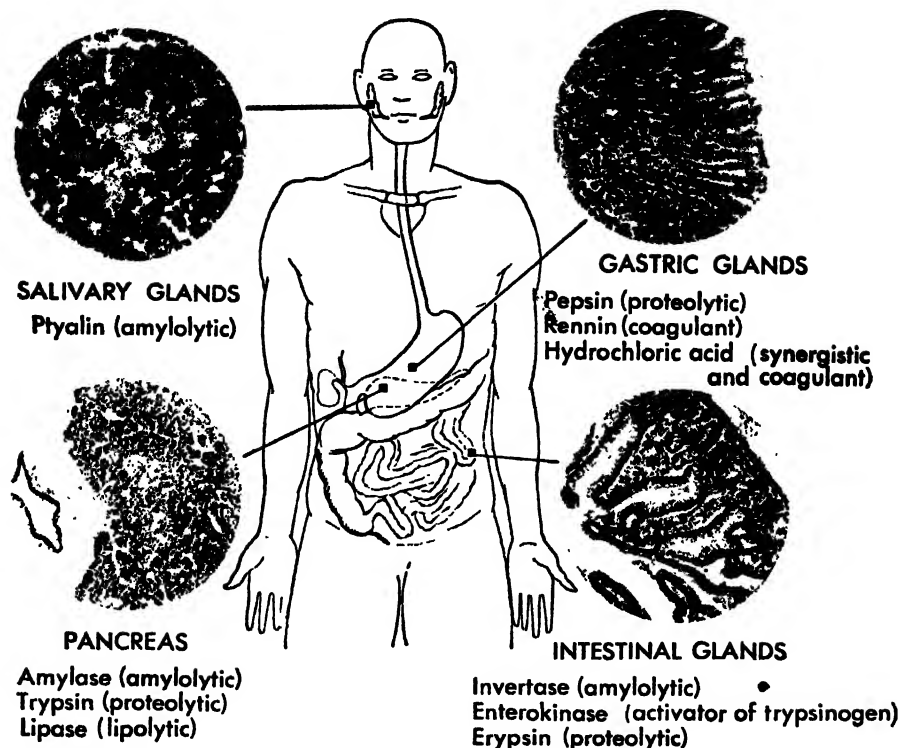
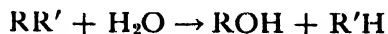


FIGURE 20.1. Origin of Digestive Enzymes. Courtesy Parke, Davis & Company.

(enzymes) for the purpose. The breaking down is generally a hydrolysis, i.e., the taking up of water followed by the splitting of big molecules into smaller ones, as shown by the general equation:



R and R' are characteristic groups which make up carbohydrate, fat, or protein molecules. The RR' molecule is of course a simplified example, and food molecules in general contain more than two such groups. Starch or protein molecules may contain dozens or hundreds of R groups. Similar hydrolyses take place outside the body, a familiar one being the formation of glucose from starch (page 368).

Food in the Mouth. The chemical changes which accompany digestion take place when various fluids from the body come in

contact with the food. The first such fluid to react is the saliva of the mouth. The body makes about three pints of this substance daily, and while it is nearly all water—better than 99 per cent—it also contains small amounts of organic and inorganic materials. Among the former is the enzyme *ptyalin*, capable of bringing about the hydrolysis of starch to simpler carbohydrates, in fact all the way down to reducing sugars, if enough time is allowed. But food is generally held in the mouth for such a brief period that even such finely divided forms of starch as mashed potatoes are not usually acted upon to a very large extent before being swallowed. Probably most of the action of *ptyalin* occurs in the stomach.

Food in the Stomach. When food passes to the stomach that organ supplies chemical substances which mix with it and cause a breakdown of large molecules into smaller ones. It also holds the food for a sufficient time so that these changes can take place. However, no significant quantity of food is absorbed into the system from the stomach.

Among the substances generated by the stomach, hydrochloric acid is of interest. This chemical is formed in the parietal cells in the surprisingly high concentration of about 0.6 per cent, although it then quickly mixes with other fluids which decrease its acidity to one third of this value or less. The mixture of hydrochloric acid and other fluids is known as *gastric juice*. Two important enzymes present in this mixture are *pepsin* and *rennin*. Pepsin catalyzes the breakdown of proteins into smaller (but not small) molecules. Rennin acts upon milk, forming clots with the casein and the calcium ion present known as calcium paracaseinate. Rennin is especially plentiful in the gastric juice of infants. The enzyme is also formed by animals, and that obtained from calf stomachs is of commercial value in the manufacture of cheese. Pepsin and the acid in the stomach also curdle milk.

The function of the hydrochloric acid in the stomach appears to be to activate the pepsin, since the latter substance splits

proteins best in an acid medium, and indeed, becomes totally inactive if made somewhat alkaline.

Food in the Small Intestine. The protein breakdown by acid pepsin in the stomach does not proceed far enough to give small, absorbable molecules before the mixture of food, saliva, and gastric juice passes through the pyloric sphincter into the small intestine. Here the mixture comes in contact with three other fluids, one formed in the pancreas (pancreatic juice), another in the gall bladder (bile), and a third from the intestine itself (intestinal juice). A number of enzymes are present in these fluids, particularly in the pancreatic and intestinal juices, and these cause the splitting of proteins, carbohydrates, and fats¹ into molecules small enough to pass through the intestinal wall. The bile, a golden yellow fluid, has a number of functions, an important one being the emulsification of fats and fatty oils. This step not only prevents the latter from coating other food particles to the exclusion of enzymes but it also puts fats and oils in a finely divided state in which they themselves are more readily acted upon by fat-splitting enzymes.

Although absorption of simple molecules such as alcohol, glucose, or some drugs is possible in the mouth or stomach, food is practically all taken in through the wall of the small intestine. This portion of the alimentary canal has a large surface (about 10 square meters) because of its irregular, folded nature, and during the time it retains its food (about five hours) there is ample opportunity for assimilation. Several million tiny projections on the inside surface of the small intestine (villi) are of great importance in the absorption process. Each villus is so constructed that digested food can pass through it to the blood stream.

PRODUCTS WHICH PASS THROUGH THE INTESTINAL WALL

Carbohydrates, Fats, Proteins. Carbohydrates are generally hydrolyzed to six carbon sugars, chiefly glucose, before absorp-

¹ A controversial point, however. There is evidence that some fat, at least, is absorbed without being split (hydrolyzed) to glycerine and fatty acid.

tion. Fat is thought to be absorbed as such, after emulsification by bile salts and fatty acids. Proteins are broken down by enzyme action to simpler and simpler molecules (proteoses, peptones, polypeptides, amino acids). Amino acids and simple polypeptides are then absorbed into the blood stream. Examples of amino acids are shown on page 391. It is important that protein foods be broken down to smaller units before absorption, because most proteins themselves are injurious if they get into the blood, and severe symptoms may result (anaphylactic shock). The sensitivity of some individuals to certain foods, i.e., eggs, milk, etc., may be caused by passage of foreign proteins from these foods into the blood stream, for some reason, before they have been split further.

Inorganic Components. Along with absorbed organic food molecules various inorganic ions and molecules will pass through the intestinal wall. Chief of these is of course water, but in addition a number of other elements must be taken in if the body is to maintain a state of health.

The element *calcium* is highly important to the body. One of its chief uses is in bone formation, since dry, marrow-free bone is over half calcium phosphate and carbonate. Calcium ion is also a necessary component of the blood serum; a minimum of about 7 milligrams of the element must be present in each 100 ml. of normal serum. Calcium ion concentrations lower than this may lead to a state of tetany (muscle contraction). Blood calcium tends to be low, and must be maintained by increased intake, during the latter stages of pregnancy.

Sodium is a required component of body fluids, being present in ionized form chiefly as chloride and bicarbonate. About 0.1 mol of sodium chloride must be present per liter of blood. When it rises above this because of excessive salt consumption it is excreted through the kidneys, and if it falls because of salt loss in perspiration and other fluids characteristic symptoms appear (page 134). The chloride ion is necessary for making hydrochloric acid in the stomach. Sodium bicarbonate in ionized form is present in the blood. The bicarbonate ion is formed from the

carbon dioxide resulting when food molecules are oxidized, and carbon dioxide is carried to the lungs chiefly as this ion.

Other metal ions are required in the body. *Iron* is a necessary element since it is part of the hemoglobin molecule, and a deficiency causes anemia. However, adults require in the neighborhood of only ten milligrams per day, and the element is present in so many foods that a deficiency is unlikely with a normal diet. Animal organs, as heart, liver, and kidneys, are particularly rich in iron. Milk is very low in iron content, but most new-born animals have a sufficient excess of the element to get them through the period in which milk is their only food. *Zinc* is apparently a necessary component of the hormone insulin. It is also present in the pancreas where insulin is formed. Small amounts of *potassium*, *magnesium*, *manganese*, *copper*, and *cobalt* are also needed in ion form for the satisfactory completion of different enzymatic processes.

The nonmetals *phosphorus*, *nitrogen*, *sulfur*, and *iodine* are indispensable in the diet, in addition to the *carbon*, *hydrogen*, and *oxygen* always present in organic food molecules. *Phosphorus* is one of the chief elements in bone, being present as calcium phosphate. It is also found in all cells as part of some proteins and other molecules. Phosphate ion also occurs in body fluids, and this radical is present in some of the compounds formed during the oxidation of muscle glycogen. Phosphorus compounds, too, play an important part in muscle contraction and relaxation. A phosphorus deficiency in the diet is not common, since the element is certain to be part of all consumed plant and animal cells. *Nitrogen*, also, is not likely to be deficient, since all ingested proteins contain it. The body normally has an excess of nitrogen, above that required for the building of proteins, which is excreted in the urine, largely as urea. *Sulfur* is needed in the formation of many proteins, but it, too, is commonly taken in in excess, partly as sulfate ion in water and partly as the organic sulfur assimilated from consumed proteins which contain the element. *Iodine* is very necessary in the human body in tiny amounts for making the hormone *thyroglobulin*. A deficiency of iodine leads to endemic goiter.

THE FOOD AFTER DIGESTION

Carbohydrates. Carbohydrates are broken down before intestinal absorption to simple sugars, the chief of which is glucose. This substance is partly transported to the body's cells and used there, furnishing energy in the process of being oxidized. But any excess of sugar goes to the liver, where it is converted to the sugar reserve of the animal, *glycogen*, or animal starch.



Note the similarity between this process and the storage of starch by plants. By means of a complex mechanism not thoroughly understood the healthy body keeps the sugar content of the blood between about 70 and 130 milligrams of sugar per 100 ml. of blood, even though much or little carbohydrate is consumed. This relatively steady state is largely governed by the rate at which glycogen forms or is used up in the liver, and this is influenced by various catalyst-like substances, chiefly insulin, which depresses blood sugar (glycogen forms faster) and adrenaline, which stimulates its production (glycogen used up faster).

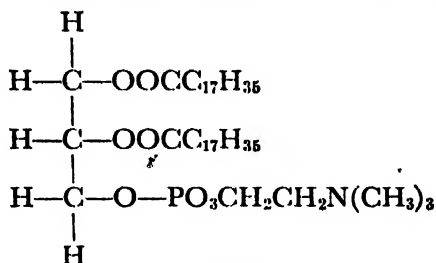
Sugar is also taken up by the muscles, and converted there to another form of glycogen (muscle glycogen). This substance is then oxidized during periods of muscular activity, in a complicated enzymatic process involving many steps, some of which appear to be similar to those which take place during the fermentation of sugar to alcohol. The energy resulting from carbohydrate oxidation to carbon dioxide and water is thought to be transferred to the muscles largely by the substance adenosine triphosphate.

The oxygen required for this carbohydrate oxidation is carried by the blood from the lungs to the tissues, as described below. The carbon dioxide formed is carried by venous blood to the lungs and released. Venous blood has enough bicarbonate ion in it to account for about 55 ml. of carbon dioxide gas per 100 ml. of blood, while arterial blood contains on the average the equivalent of about 50 ml. of carbon dioxide per 100 ml. of blood.

Fats. After passage through the intestinal wall fats are in part oxidized as food, in part converted to chemical substances which are required in cell protoplasm (lipids), and in part stored as fat.

The portion used for energy is oxidized, like glucose, to carbon dioxide and water. When fat is consumed in this manner much more energy is liberated than in the oxidation of carbohydrates, more than twice as much when equal weights of the two are compared. This is because the carbohydrates are already partially oxidized at the start of the process, i.e., they contain more oxygen than fats. Moderate work can be carried on using fat as the energy source. However, for strenuous muscular work, carbohydrate oxidation is apparently the chief or preferred source of energy, and fatigue is apparent much sooner on a high fat diet under these conditions than on a high carbohydrate diet.

The fat used to form essential substances in the cell protoplasm is altered to various more complex molecules which, however, retain in part their structures as esters. The lecithins are examples.

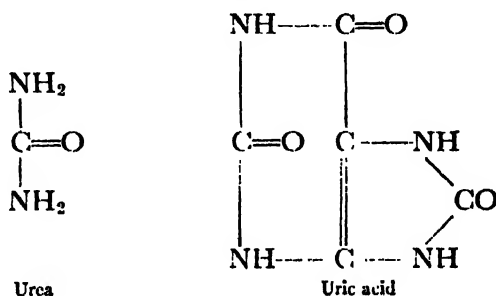


An α Lecithin

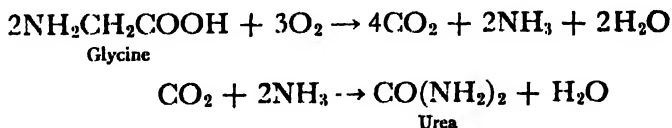
Excess fat, beyond that used for food or essential protoplasm substances, is stored in fatty deposits. These serve two useful functions. They furnish protective and insulating layers around organs, such as the kidneys and the uterus, which are susceptible to injury from external sources. They are also available for energy, in case the food intake of the body should become insufficient for any reason. Fat deposits in excess lead to obesity. This is practically always caused by the taking in of excess fats and carbohydrates, the latter being changed to fat when the liver and muscles are unable to store more glycogen. Glandular disturbances account for only about 1 per cent of obesity cases.

Proteins. The amino acids formed from protein foods by enzyme action in the small intestine are also carried by the blood to all regions of the body, where they are in part burned up, in part synthesized into protein cell material and in part converted to carbohydrates and fats. Let us consider these various changes in greater detail.

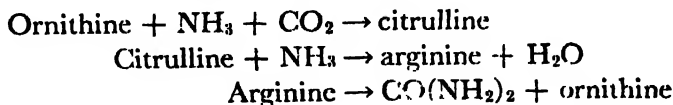
When amino acids are oxidized they furnish approximately the same amount of energy as a similar weight of carbohydrates. The oxidation products are carbon dioxide, water, and nitrogen compounds, chiefly urea in humans, and uric acid in birds, snakes, and lizards. While the product excreted by humans is



chiefly urea, it is thought that ammonia is first formed, then urea from this. Thus with the amino acid glycine:



It is thought that the amino acids ornithine, citrulline, and arginine probably take up carbon dioxide and ammonia and give off urea in the cycle shown below.



Proteins are continually being resynthesized in the body. At one time it was thought that body proteins once formed were there to stay, while ingested proteins were burned up, or converted to other types of molecules. But it has been shown by use

of molecules containing tagged (isotopic) nitrogen atoms that there is a continual breaking down of body proteins followed by their resynthesis from the amino acids resulting from enzyme action upon consumed food proteins. In experiments with rats, the internal organs, such as heart, kidneys, and intestinal tract, were found to have taken up the tagged nitrogen to the greatest extent, indicating a higher protein rebuilding rate at those places.

THE BLOOD

Composition. About 9 per cent of the weight of a human being is blood. This fluid substance flows in a nearly closed system in



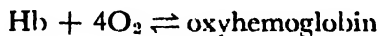
FIGURE 20.2. Normal Blood Smear. Many red corpuscles are visible. The irregular body with a dark center is a white blood cell. Small bodies are platelets. Courtesy Parke Davis & Company.

the body—the vascular system—and while there is ample opportunity for passage of materials through cell walls into and away from the blood, it actually comes in contact with but few of the tissue cells, except in the spleen and the liver. The blood is a suspension of microscopically visible units (red and white corpuscles and platelets) in plasma, the latter being itself a complex dispersion of large, intermediate, and small molecules and ions in water. The corpuscles and platelets comprise 40 to 45 per cent of the blood

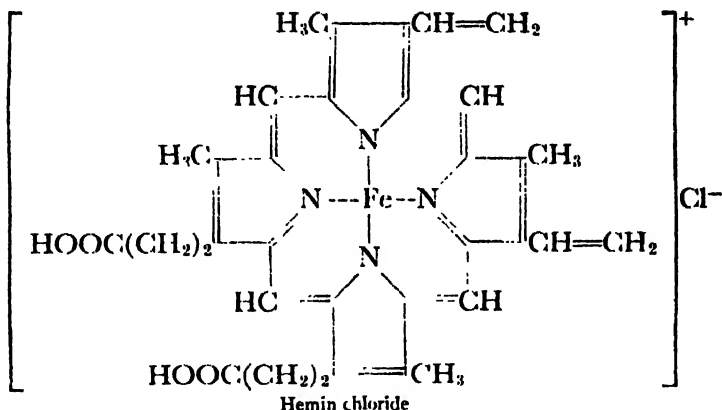
and the plasma the remainder. Water is the chief molecular substance present. It makes up some 90 per cent of the plasma and about 65 per cent of the red blood cells.

Erythrocytes. Red blood corpuscles, or erythrocytes, consist almost entirely of water and the conjugate protein hemoglobin. These cells do not appear to be living things, i.e., they have no nuclei, nor do they divide. Their chief function appears to be

the carrying of oxygen from the lungs to the neighborhood of the tissues in which oxygen is needed for the oxidation of carbohydrates, amino acids, and fats. This is accomplished by the hemoglobin, which forms with oxygen in the lungs a loosely bound compound known as oxyhemoglobin. This in turn breaks down in the tissues in regions of low oxygen concentration to hemoglobin and oxygen. The formation and decomposition of oxyhemoglobin can be written by using the abbreviation Hb for the giant hemoglobin molecule.



The hemoglobin molecule consists of the protein globin attached to a complex ion known as *hemin*, shown below.



The taking up and liberation of oxygen, which occurs very rapidly, is apparently influenced largely by the hemin part of the molecule. There is a considerable similarity between this ion and the chlorophylls (page 413).

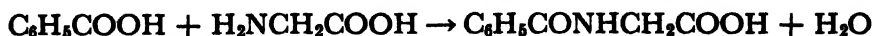
Other Blood Components. Blood contains white corpuscles, or leucocytes. Unlike the red cells, these appear to be single-celled organisms, and are chemically much more complex than the red cells. Several kinds exist, but in total they are far outnumbered (about 1000 to one) by the red cells. Blood also contains platelets. These are smaller than corpuscles, and appear to be utilized in the clotting of blood. (See Figure 20.2.)

Blood plasma is chiefly water. Of the 10 per cent solid material it contains, most of this is proteins (seven tenths), while the remainder consists of food molecules on their way to be used or stored, waste products such as urea, and chloride, bicarbonate, phosphate, and sulfate salts of the metals mentioned earlier, in ionized form. There are also things with special functions, enzymes, antibodies, etc.

Blood Clotting. One protein, present in the blood plasma to the extent of about 0.3 per cent, is the substance *fibrinogen*. This is responsible for the clotting of blood. Fibrinogen is thought to be made in the liver, or its production is controlled in some way by this organ. The clotting of blood is thought to require a very complicated series of reactions. According to one view, the clotting of blood is thought to be due to destruction of a trace of *heparin* in the blood by substances present in the wound—perhaps, substances obtained from the blood platelets. Fibrinogen thereupon reacts with a calcium-containing enzyme, *thrombin*, to form the insoluble, clotting protein, *fibrin*. It is interesting to note that, first, calcium ion is necessary for the formation of thrombin, and therefore for clotting, and in its absence clots do not form, and secondly, addition of heparin to blood will also inhibit clot formation. Heparin has been used in some types of surgery where there is danger of internal blood clot formation. Other substances are also used to inhibit blood clotting, notably dicoumarin.

Blood Defenses. Blood contains substances which aid in overcoming harmful products which enter it. While the changes which take place are undoubtedly chemical in nature, they are usually of such complexity that they can be described only in terms of units larger than molecules. The white blood cells, for example, are thought to react with dead cells, or with entering bacteria, probably because of the presence of enzymes which break down these things into smaller molecules which then either serve as building units, or food, or are excreted. Sometimes a more soluble product is formed which can be more

readily excreted. Thus, benzoic acid is acted upon by glycine to form the somewhat more soluble hippuric acid.



Antibodies should also be mentioned under the heading of blood defenses. Foreign, protein-like substances, known as antigens, are given off by invading pathogenic organisms. An antigen is thought to consist of a protein having attached to itself a non-protein part (hapten) which may be different for different organisms. When this type of molecule is introduced into the blood stream, chemical changes take place which result in the production of what might be termed a new type of defense molecule by the blood. This has the ability to react with the antigen and precipitate it, causing its removal from the blood stream. The new blood molecule is thought to react specifically with the hapten part of the antigen. The defense molecule so made by the blood is known as an antibody or an antitoxin.

Many antibodies are proteins of the serum globulin type. After their formation the system becomes sensitive to the antigen, and further quantities are quickly precipitated. In other words, immunity has been established for the particular organism. Antibody formation is induced either by an attack of the disease in question or by allowing the antigens themselves to come in contact with the blood stream (i.e., smallpox vaccination). Also antibodies may be formed in an animal or in another person and then injected (as diphtheria antitoxin from the horse,



FIGURE 20.3. Determining Carbon Dioxide Combining Power of Blood. Courtesy Parke Davis & Company.

or whooping cough serum from a person who has just recovered from that disease).

The first injection of a foreign protein into the blood may not produce a marked reaction, but the sensitivity which is then built up, i.e., the antibodies, cause extreme reactions if the same foreign protein is injected several weeks later, and serious or fatal reactions may follow (anaphylaxis, allergy, foreign protein reaction). The science of immunology, spread over the fields of medicine, bacteriology, and chemistry, deals with antigens, antibodies, and related phenomena.

Temperature and the Blood. Another important function of the blood is in helping to control body temperature. Since heat is generated by the oxidation of food molecules, a completely insulated human body would therefore become hotter and hotter as long as these processes took place. Such a condition is avoided by loss of heat from the body's surface, including the lung surface, and this is where the blood becomes of importance.

The small blood vessels near the surface of the body have the property of dilating or constricting, and in fact they do both in a rhythmical manner. When body temperature tends to become too high they remain dilated much longer than they remain constricted, i.e., the rhythm pattern changes to bring about this condition. Blood then flows through these dilated vessels in greater amounts and is cooled by coming in contact with the cooler outer portions of the body. Perspiration may have helped cool these outer portions by its evaporation. In cold weather, on the other hand, when body temperature tends to become subnormal, these surface vessels dilate much less frequently, less blood is cooled at the surface, and most of the blood is kept well within the body. However temperature control of the body involves much more than this, since it includes temperature receptors in the skin, to enable the seat of temperature control (probably in the hypothalamus section of the brain) to set in motion the cooling off or warming up mechanisms. The

latter include shivering, the urge to exercise when the body is cold, and to take in hot stimulating food and drink, so that the rate of food oxidation in the muscles will increase.

Life Span of Blood Cells. Red blood cells have an average life of from three to four months. They are then absorbed, largely in the spleen and the liver, and decomposed. The hemoglobin is thought to change in the process to the reddish pigment bilirubin, which is the chief coloring matter in bile.

THE LYMPH

Another body fluid, different from blood in that it has no red blood cells and a lower protein content, is the *lymph*. This liquid bathes the tissues and is also in contact with the blood, so that substances which the blood must transport to the tissues pass from the blood to the lymph. Waste products go through the same process in reverse. The lymph occupies a special system of vessels known as the lymphatics. Lymph from different parts of the body may vary somewhat in composition. The various special fluids in the body, such as that in the cerebrospinal region, the eyeballs and the joints, can be regarded as modified forms of lymph.

THE BONES

Bone is a mixture of organic and inorganic matter. Dry, marrowless bone is more than half mineral matter, chiefly calcium phosphate and carbonate in the molar ratio of about two to one. The other part of dry, marrowless bone is mainly the substance collagen, from which is obtained gelatin by hydrolysis. Living bones contain up to about one-fourth water.

The inorganic, calcium phosphate-carbonate part of bone is deposited in crystalline form, and cannot be regarded as living matter. However, it is in active contact with living matter, and can be dissolved, putting calcium and phosphate ions into the body fluids, or deposited out from body fluids, if body needs require these changes.

THE MUSCLES

Muscle cells, with their unique property of contracting and relaxing, are among the most significant and interesting components of living organisms. The portion of the cell which brings about the change in shape—the muscle fiber—is thought to be part of the cell nucleus. Each fiber is composed of smaller units, the fibrils, which in turn are made up of still smaller filaments. The latter appear to consist of thread-like molecular complexes which are chiefly the proteins myosin and actin in combination (actomyosin), and the nucleotide adenosine triphosphate (ATP). This protein-organic phosphate composition is not unlike that of cell nuclei in general, but in muscle cells the smaller nucleotide ATP apparently takes the place of the large nucleic acid molecules normally present. The thought has been expressed that this streamlining is an evolutionary response to the need for a structure which will operate with fewer frictional effects.

Myosin is the most abundant building unit present. It is a protein which forms rod-shaped molecules with a molecular weight of approximately 900,000. Present in smaller amount is the other protein actin. This substance by itself in vitro is unique in that it can exist in two strikingly different forms. In salt-free aqueous solutions it forms a colloidal suspension in which it is present as globular particles (G-actin). But when salt is added it changes to a fibrous form (F-actin) and causes the suspension to become highly viscous. Szent-Györgyi (Hungarian) showed in a dramatic experiment that when a combination of actin and myosin was extruded into salt solution in the form of an insoluble thread, the latter contracted when treated with ATP, i.e., an event similar to muscle contraction was caused to take place in vitro.

No simple explanation of the muscle contraction-relaxation cycle appears possible at this writing (). The most recent hypothesis seen by the writer is that of Mommaerts,² to the effect that resting muscle, upon stimulation, reacts with ATP, changing from a combination of G-actin and myosin to a contracting

combination of F-actin and myosin (actomyosin). In the reaction ATP forms adenosine diphosphate (ADP). Loss of phosphate by ATP releases much energy, and this is used in doing the work involved as the muscle contracts. The energy lost is thought to be restored by rephosphorylation of ADP, perhaps by phospho-creatine. This in turn is reformed with the aid of energy obtained during the oxidation of muscle glycogen.

ENZYMES

The cells and fluids of the human body (and all other living matter) contain a great many types of giant molecules, perhaps numbering in the thousands, which catalyze the various chemical reactions which take place therein. These substances are known as *enzymes*, and each has the function of speeding up the reaching of equilibrium in a certain specific chemical process. Very little is known about most of these, but of the ones which have been studied some appear to consist of a protein to which is attached another different and smaller group (the prosthetic group) which aids in determining the specificity of that particular enzyme. It appears that at least some of the vitamins and perhaps the hormones discussed below are molecules which make these prosthetic groups, or are closely related to them. The need for vitamins and hormones becomes clear if this is the case, since in their absence some necessary chemical change in the body fails to take place.

Thus, enzymes catalyze the hydrolysis of large food molecules to small ones, as starches to sugars and proteins to amino acids. The formation of glycogen, and its change to pyruvic acid in the muscles, is the result of the catalytic action of some 20 different enzymes. This process has been very carefully studied, and has been duplicated, with purified enzymes, outside of the body. It appears that there is a different enzyme for every type of reaction in the intermediary metabolism of the body.

The name given enzymes is usually that of the substance acted upon, together with the ending *-ase*. Some enzymes are given in Table 20.1.



FIGURE 20.4. Apparatus for Purification of Insulin. Courtesy Eli Lilly & Company.

As our knowledge of enzymes grows, it begins to be apparent how this field and other fields of quite a different nature are related. For example, biologists have demonstrated rather clearly that individual genes control the production of individual enzymes, linking together the fields of genetics and enzymology.

TABLE 20.1 Some Enzymes and Their Substrates

<i>Enzyme</i>	<i>Substance acted upon (substrate)</i>
UREASE	Urea
SUCRASE	Sucrose
MALTASE	Maltose
ARGINASE	Arginine (an amino acid)
CARBONIC ANHYDRASE	Carbonic acid

It seems possible that some of our chemotherapeutic agents, particularly the sulfa drugs, may act as prosthetic groups which compete with the natural prosthetic groups in bacterial enzymes, thus throwing the bacteria's metabolism out of order and preventing reproduction. If this is so there will be a further tie-up between the fields concerned.

H O R M O N E S

Certain chemical substances are released to the body by glands which are without ducts (the endocrine glands), by the passing

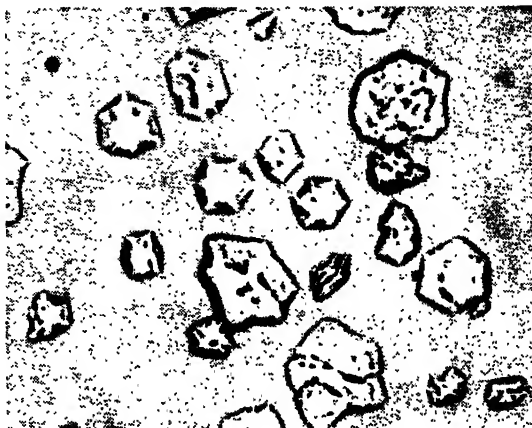


FIGURE 20.5. Zinc Insulin Crystals, Magnified. Courtesy Eli Lilly & Company.

of the substances, through some sort of semipermeable membrane, directly into the blood stream. These are the *hormones* (from the Greek *hormao*, "I arouse"). They are present only in small quantities in the body, but are highly necessary for proper growth and normal operation. Hormones are related in some way to enzymes, but whether they are enzymes, or merely influence the behaviour or synthesis of enzymes, is not known at the present time. When the body is in a pathological state because of a deficiency of hormones, miraculous cures are sometimes



FIGURE 20.6. Estrone Crystals. This substance is used as an estrogenic stimulant. Courtesy Eli Lilly & Company.

effected by the addition of the needed hormone to the body from without. Some of the important hormones are described in Table 20.2 on the next page.

TABLE 20.2 Some Important Hormones

<i>Name</i>	<i>Source</i>	<i>Function</i>
INSULIN	Pancreas	Limits blood sugar concentration.
ADRENALINE	Adrenal glands	Elevates blood pressure; causes more rapid hydrolysis of glycogen to blood sugar.
ADRENAL CORTEX HORMONES	Adrenal glands	Prevent escape of salt through kidneys, influence age of sexual development, prevent rheumatoid arthritis (cortisone).
SEX HORMONES	Gonads	Regulate sex characteristics.
PITUITARY HORMONES	Pituitary gland	Master hormones of the body, in that they influence behaviour of other ductless glands. Posterior hormones stimulate smooth muscle contraction, raise blood pressure, control urine volume. Anterior hormones regulate growth. ACTH stimulates adrenal cortex to produce cortisone.
THYROGLOBULIN	Thyroid gland	Controls metabolic rate.
PARATHORMONE	Parathyroid glands	Governs calcium and phosphate ion concentration in the blood.

VITAMINS

A group of substances which the body needs, but cannot itself synthesize, is the *vitamins*, so named because in the early years of vitamin research they were thought to be amines necessary for life (vital amines). Later it was found that for the most part they were not amines, but the name vitamin had become fixed nevertheless. Vitamins are furnished by plants, including yeast, and by various animal organs, and today they are in part made synthetically. They are present in adequate amount in a properly chosen diet, but in cases of deficiency they can usually be supplied more surely in concentrated, capsule form. Vitamins are intimately linked in some manner with the body's enzymes, and there is increasing evidence that the prosthetic group of some enzymes (which in part determines their specificity) is either a

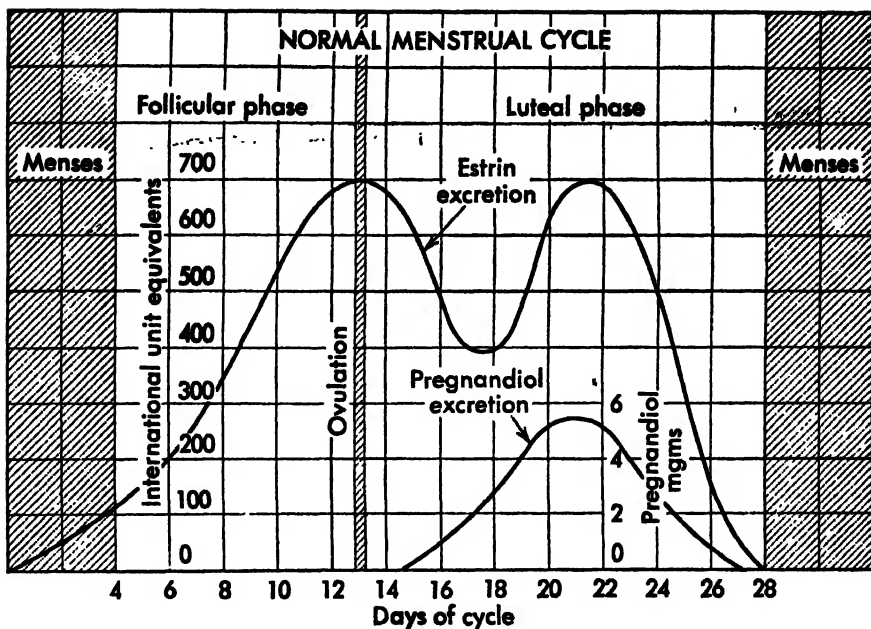


FIGURE 20.7. Female Sex Hormone Excretion. Urine analysis indicates that estrin and pregnanediol excretions reach maxima as shown, the first accompanying ovulation and the second coinciding with maximal corpus luteum activity. Courtesy Parke Davis & Company.



FIGURE 20.8. Thiamin, or Vitamin B₁ Crystals, Magnified. Courtesy Merck & Co., Inc.

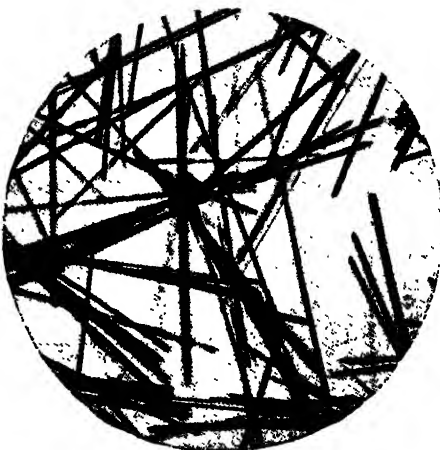


FIGURE 20.9. Riboflavin, or Vitamin B₂ Crystals, Magnified. Courtesy Merck & Co., Inc.



FIGURE 20.10. Ascorbic Acid, or Vitamin C. Magnified crystals. Courtesy Merck & Co., Inc.



FIGURE 20.11. Vitamin B₁₂ Crystals, Magnified. Courtesy Merck & Co., Inc.

vitamin or a substance closely related to a vitamin. Some important vitamins are given in Table 20.3.

CHEMOTHERAPY

The treatment of infectious diseases by internal or external use of specific chemical substances which kill or inhibit the growth of the pathogenic organism causing the infection is known as *chemotherapy*. This branch of medicine has become of such importance since that substances like penicillin and the sulfa drugs are now common topics of conversation in the home. Interest is greatest at the present time in two classes of therapeutic agents, those synthesized in the laboratory and those produced by living microorganisms (antibiotics).

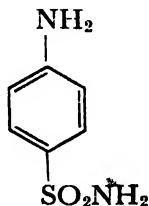
Synthetic Chemicals Used in Chemotherapy. The sulfa drugs are the best-known synthetics used for chemotherapy.

TABLE 20.3 Some Important Vitamins

<i>Name and discoverer*</i>	<i>Source</i>	<i>Function</i>
Thiamine (B ₁), Williams, American,	Rice. Now synthesized	Prevents polyneuritis or beriberi
Riboflavin (B ₂ , G), Karrer, Swiss,	Liver, heart, kidneys	Prevents ariboflavinosis
Nicotinic acid (Niacin), Elvehjem, American,	Meat, yeast. Now synthesized	Prevents pellagra
Vitamin A, Karrer, Swiss,	Cod-liver oil, egg yolks, butter	Increases growth rate, resistance to disease. Prevents night blindness
Ascorbic acid (C), King, American, Szent-Györgyi, Hungarian,	Fresh fruits and vegetables	Prevents scurvy
Vitamin D, Windaus, German,	Fish oils. Action of UV light on ergosterol	Prevents rickets
Vitamin K, Dam, Danish,	Green plants	Prevents hemorrhaging
Vitamin B ₁₂ , Smith, English and an American group at Merck Laboratories,	Liver	Prevents pernicious anemia

* The discovery of the source, function, formula, and synthesis of the vitamins involves many more scientists than are mentioned here. Space permits only a few prominent names.

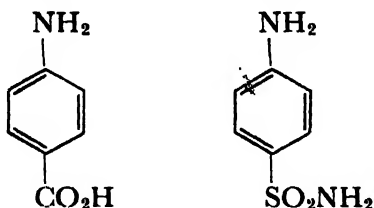
Sulfanilamide was the first of these compounds, shown to be effective against such sphere-shaped bacteria as streptococci and staphylococci. Prepared from aniline, C₆H₅NH₂, it has the formula:



Later it was found that related compounds were less toxic to humans than sulfanilamide. These derivatives were made by substituting other groups for hydrogen atoms in one or both

NH₂ groups of sulfanilamide. This led to such substances as sulfathiazole, sulfapyridine, sulfathalidine, sulfamerazine, sulfaguanidine, and sulfasuxidine.

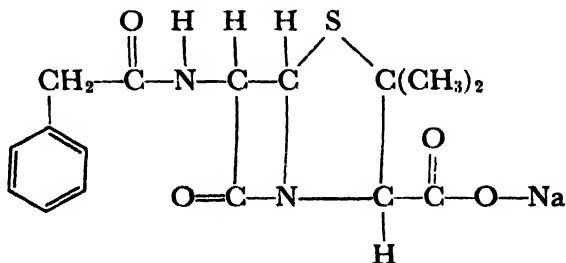
It is not known for sure how the sulfa drugs work, but the generally accepted theory at the present time is that the bacteria cannot distinguish these molecules from *p*-aminobenzoic acid.



p-aminobenzoic acid is part of the vitamin B complex needed for proper bacteria metabolism; in its absence, as when sulfa drug molecules are taken up instead, bacteria cannot reproduce.

The sulfa drugs do not help in overcoming virus infections, or such diseases as tuberculosis or typhoid fever, but they have saved the lives of many people suffering from pneumonia, meningitis, and blood stream infections.

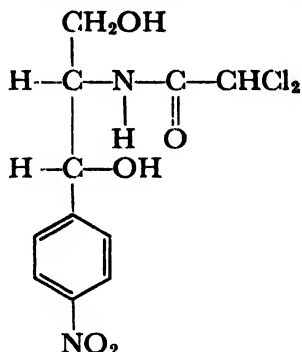
Antibiotics. These are complex organic substances, produced by microorganisms, which destroy or inhibit the growth of many pathogenic bacteria. The penicillins are probably the least toxic (to humans) of the antibiotics known to date. Six of these have been isolated, the most effective being penicillin G. The structure of the sodium salt of penicillin G is probably that shown below.



Penicillin is made inactive by gastric juice, hence it must be administered in some way other than through the stomach, such

as intravenously, intramuscularly, etc. Frequent and massive doses are possible because of the low toxicity of the sodium salt, and indeed, these are often necessary, since the substance is rapidly excreted from the kidneys when given in simple solutions (50 per cent in an hour).

Chloromycetin is an antibiotic which was obtained originally from soil bacteria. It is now synthesized. The substance is unusual in that it can be considered as a derivative of both nitrobenzene and dichloroacetic acid (see formula), two substances



never before associated with life. Chloromycetin is effective against virus pneumonia, Rocky Mountain spotted fever, typhus fever, and many other infections.

Space prohibits discussion of the hundred or more additional antibiotics known, such as streptomycin, aureomycin, gramicidin, tyrocidin, bacitracin, etc.

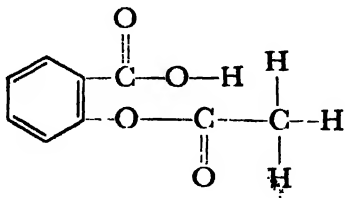
ANALGESICS

Analgesics are substances which are administered to relieve pain without causing loss of consciousness, whereas compounds like diethyl ether, which relieve pain by producing unconsciousness, are called *anesthetics*.

Aspirin. Acetylsalicylic acid, or aspirin, is the most commonly used analgesic. It has the formula shown on the next page. The various brands of aspirin tablets differ in dissolving rate, feel, or taste in the mouth, etc., not because of any difference in the acetylsalicylic acid content, but because the filler, which comprises

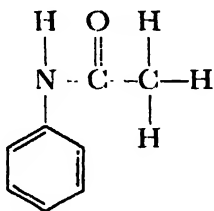
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most of the tablet, differs in composition in different brands, such substances as starch, dextrose, or clay being used for this purpose.

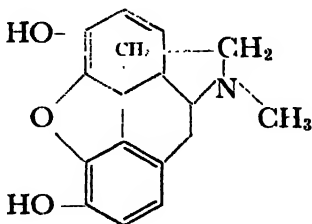


Aspirin splits in the stomach and small intestine to form acetic acid and salicylic acid; the latter substance is the active analgesic. There is recent evidence that salicylic acid lowers the prothrombin level in the blood. Since prothrombin is a precursor of thrombin, required for the clotting of blood, unsatisfactory blood clotting may take place in presence of salicylic acid. Aspirin is hence a dangerous analgesic to use following surgery, particularly tonsillectomy, unless accompanied by use of the antihemorrhagic substance vitamin K.

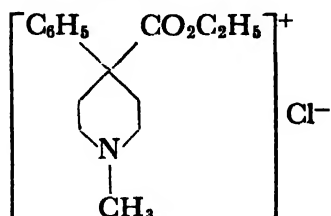
Other Analgesics. Acetanilide is another widely used analgesic. Both aspirin and acetanilide are also used as *antipyretics*, to lower fever.



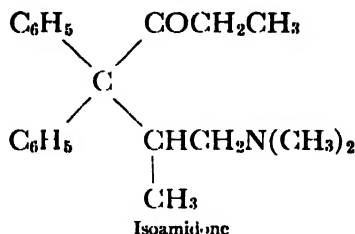
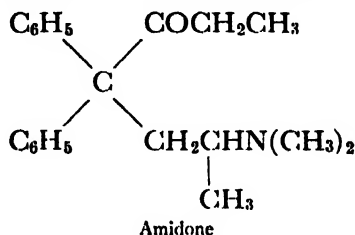
Morphine, obtained from certain varieties of poppy seed, has been indispensable as a more powerful analgesic administered



by members of the medical profession. Unfortunately its use tends to lead to addiction. A number of simpler compounds are now synthesized which in many cases make suitable, though for the most part not as powerful, substitutes for morphine. Demerol is probably the best known of these.



Amidone and isoamidone are powerful synthetic analgesics.



Many other analgesics are in use, but lack of space in a book of this type prevents further discussion of this important class of substances.

Self Study Questions

1. Discuss the action of enzymes upon food from the time it enters the mouth up to the time it is absorbed by the intestinal wall. What is the general nature of the chemical changes that take place? What types of digestive fluids act upon the food and what are their sources?

2. What metallic and nonmetallic elements are needed by the body for growth and maintenance of health? What is the function of each?
3. In what different ways are fats utilized by the body? How does the energy obtained from fat compare with that given off during the oxidation of a similar weight of carbohydrate or protein?
4. How are carbohydrates used by the body? Include in your discussion oxidation, storage, and conversion to other types of molecules.
5. What is the fate of the amino acids in the body which pass through the intestinal wall after they have been obtained by hydrolysis of proteins? What is the chief end product of oxidation of amino acids? How is it thought to be formed?
6. What are the chief components of the blood? Discuss the function of the blood (a) as an oxygen and carbon dioxide carrier, (b) as a clot former in wounds, (c) in its defense against pathogenic organisms and toxins, (d) in the control of temperature.
7. Discuss the composition and functions of (a) the lymph and (b) the bones.
8. What are the functions of enzymes in living cells? Upon what basis are enzymes named? Give some examples.
9. What characteristic type of gland generates hormones? What is the master gland of the body as far as hormone production is concerned? Give some examples of hormones and their functions.
10. How do vitamins differ in source from the hormones? Name the important vitamins and the condition which they prevent by their presence.
11. What are the meanings of the terms chemotherapy, antibiotic, analgesic, antipyretic, anesthetic. Give examples of these substances.
12. What chemical substance is needed in the blood to prevent (a) excessive clotting of blood, (b) hemorrhaging, (c) more blood sugar, (d) less blood sugar?
13. What substance is missing or deficient in the body during (a) tetany, (b) rheumatoid arthritis, (c) scurvy, (d) diabetes, (e) endemic goiter, (f) rickets, (g) pernicious anemia, (h) pellagra?

PART EIGHT

Important Products of Chemistry in Daily Life

XXI

Rubber

The familiar substance rubber has been known to the civilized world for about four hundred years, and to the natives of tropical America before that, since they were found by early European explorers to possess pieces of the crude material obtained from the exudate of certain trees. One of the first uses of the substance in Europe was as an eraser, and for this reason it came to be called rubber. The term "caoutchouc" is also employed in some countries, from words in the language of the South American Indians meaning, "wood tears," i.e., drops of liquid coming from the rubber trees after injury.

Rubber products in the early years of their use were somewhat unsatisfactory because of their great change in behaviour with temperature. They lost their elasticity in cold weather and became soft and sticky when hot; only within a rather narrow temperature range did they have satisfactory resiliency. But in 1839 Goodyear (American) discovered the process of vulcanization described later, whereby it was possible to make rubber articles with properties much less dependent upon temperature.



FIGURE 21.1. Obtaining Latex from a Rubber Tree. Courtesy The B. F. Goodrich Company.



FIGURE 21.2. Rubber Plantation Receiving Station. Coolies weighing in latex which they have collected. Courtesy The B. F. Goodrich Company.

From that time on rubber became an increasingly important substance.

Two distinct classes of rubber must be recognized, the first being the natural product and the second the various types of synthetic rubbers. These will be considered separately.

NATURAL RUBBER

Latex; Crude Rubber. Natural rubber with nearly the same properties occurs just outside the cambium layer (just under the bark) in several hundred different types of tropical plants. However, most of it is obtained from Malaya and the East Indies, from a Brazilian tree (*Hevea brasiliensis*) which has been transplanted and grown successfully in those areas. When an incision is made in the bark of these trees, a milky, somewhat viscous liquid—latex—is obtained. The chief component of latex is water, but about one-third of it is made up of tiny, separated, spherical, or pear-shaped particles of rubber, one to two microns¹ in diameter. The liquid also contains small amounts of other substances, chiefly resins and proteins.

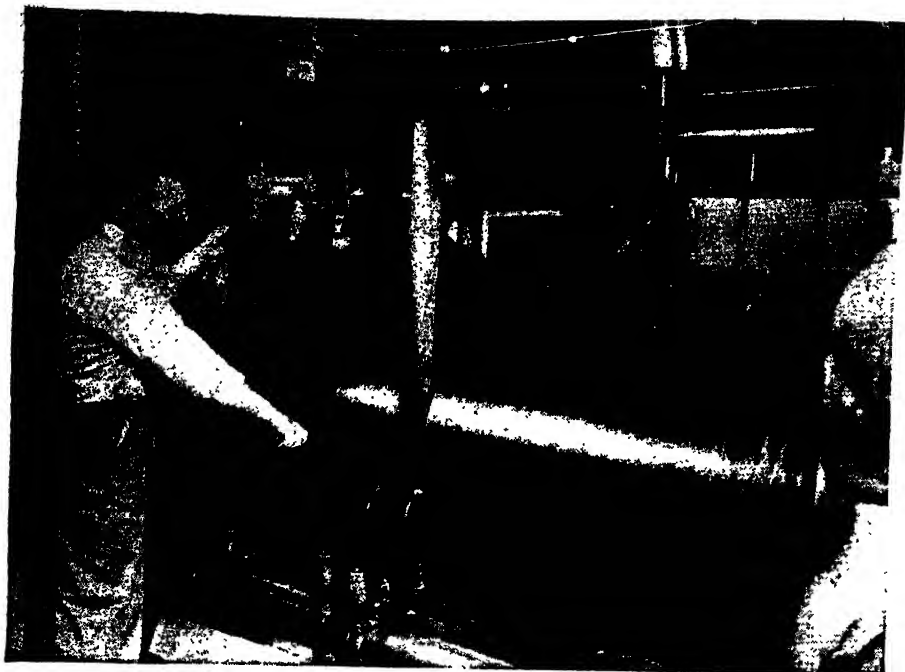
¹ One micron = 10^{-4} cm.



FIGURE 21.3. Packing Crude Natural Rubber. Courtesy The B. F. Goodrich Company.

In recent years an increasing number of rubber products have been made directly from latex, and if it is to be used in this way it is stabilized by chemical treatment, concentrated and shipped to the manufacturing center. But for other purposes the rubber is removed from the latex. This is done by coagulating it, usually with acetic acid. The rubber particles then come together and form aggregates which settle out. The spongy, cheese-like masses which result are separated from the liquid by passing them through rollers, washing and drying them. They may then be smoked, to give a product better able to resist bacterial attack. The material remaining after this treatment is crude rubber, and in this form it is shipped to the factory.

Treatment of Crude Rubber. Crude rubber is not sufficiently plastic to shape accurately, i.e., it cannot be made to flow so as to completely fill a mold. To make it into a plastic substance it is worked in a mill, or "masticated." One way of carrying out the operation consists of passing the rubber many times through a pair of rollers so geared that one roller turns faster than the other, causing a shearing action. It is believed that the mastication of rubber, effected in the presence of air, is accompanied by the



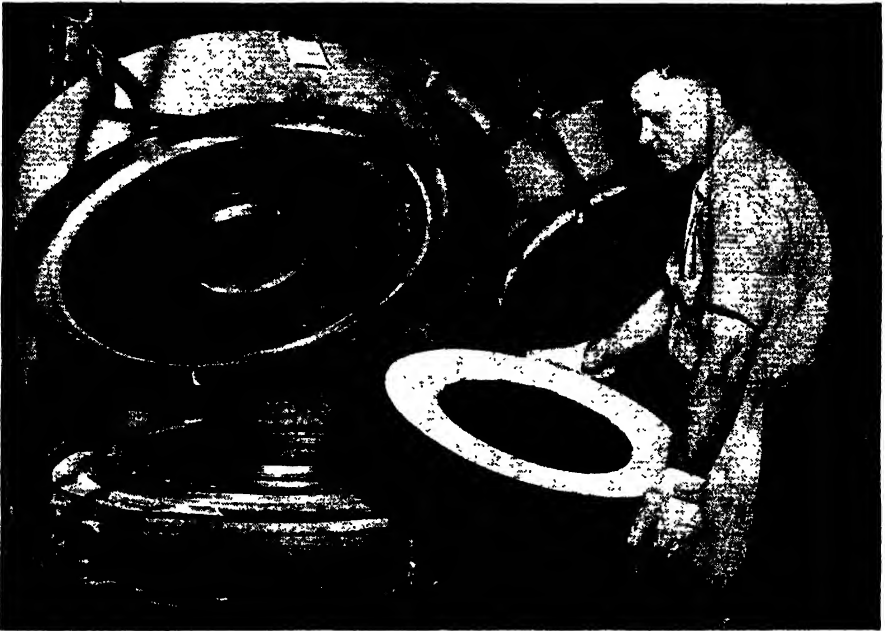
(a)



(b)



(c)



(d)

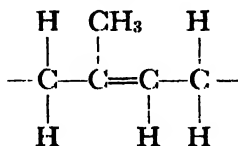
FIGURE 21.4. Tire Manufacturing. (a) Milling, (b) calendering, where milled rubber is put on tire fabric, (c) air-bagging, where the tire shape is acquired for the first time, (d) vulcanizing. Courtesy Goodyear Tire & Rubber Company.

absorption of oxygen from the air which leads to an oxidation and breaking of the long rubber molecules into somewhat shorter ones. This explains the marked increase in plasticity which results from the milling. During the latter part of the operation other ingredients are added and allowed to become thoroughly mixed in. These include sulfur, fillers, accelerators, antioxidants, and pigments. The mixture is then ready to shape and vulcanize.

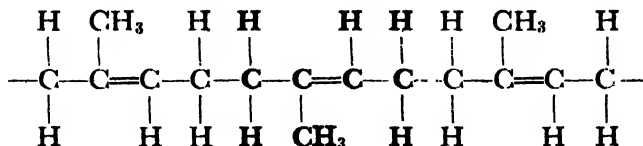
Shaping is done in various ways, commonest of which is probably by forcing the mixture into a mold. After milling, it becomes sufficiently plastic so that it will completely fill such a mold and take a sharp impression. The mold is often the type which opens into two halves and closes in a hydraulic press. When the plastic mass in the mold is heated the process of *vulcanization*, discussed below, takes place. As the result of vulcanization the rubber loses its plasticity but gains in elasticity or "bounce." The vulcanized rubber furthermore exhibits a much better resiliency at high and low temperatures.

This has been a brief account of how liquid from the rubber tree is made into a useful rubber article. Let us now examine the chemistry involved in these changes.

The Rubber Molecule. The hydrocarbon molecules which largely make up the tiny rubber particles in latex are very long in one direction (if stretched out), like cellulose molecules, and consist of a large number of C_5H_8 building units joined together. The building unit structure is shown below.



These units are combined in a rubber molecule, as shown in the drawing below.



Substances whose molecules consist of many repetitions of such building units are known as *polymers*. The polymer molecules which make up rubber are all long, but they differ in size, i.e., some are longer than others. Rubber can then be thought of as having the formula $(C_5H_8)_x$, where x is large but variable.

In unstretched rubber these long molecules are not straight, nor are they arranged according to any pattern. Rubber is therefore an amorphous solid in the unstretched state. Scientists picture a molecular arrangement somewhat like a mass of string made up of many hopelessly snarled pieces. The bending which the rubber molecules must undergo to form such a mass is thought to be possible because the angle which any one of the carbon atoms in the chain makes with two adjacent atoms is less than 180° , and because of the free rotation of parts of a molecule around single bonds (page 336).

It is not difficult to understand the ability of rubber to stretch. This can be explained by the shifting of molecules and parts of molecules to new positions in which they tend to become parallel with each other, their long axes corresponding to the line of stretching. If this is what happens, stretched rubber must become somewhat crystalline in nature, with parallel molecules. The experimental evidence bears this out, since stretched rubber gives an X-ray diffraction pattern of the type characteristic of crystalline substances, while the pattern of unstretched rubber is that of an amorphous material.

The property of rubber which is more difficult to explain is its recovery after stretching. Most substances, after being pulled out to several times their original length, either break or remain in an elongated state, as would be the case with wire or taffy, for example. The ability to return to, or nearly to the starting shape after stretching, described by the word *elastic* or *resilient*, is what makes rubber and other elastomers unique substances. There is some uncertainty as to the fundamental mechanism which accounts for elasticity. Perhaps in the process of stretching and of straightening molecular chains there is caused an actual change in the angle which carbon atoms make with neighboring

pairs of atoms. This would set up a condition of strain which would serve as a restoring force.

Vulcanization. Vulcanization is usually considered to be the process of heating rubber with sulfur. As a result the tensile strength of the rubber is increased many times, the elasticity is



FIGURE 21.5. Inner Tubes for Tires. The rubber compound for inner tubes is extruded through a die to form the tubing in its proper thickness and diameter. Courtesy The B. F. Goodrich Company.

much improved, and the plasticity (of the milled rubber) diminished, so that the article does not readily undergo permanent changes in shape when deformed. After vulcanization, the elasticity is much less affected by temperature and there is a marked decrease in the solubility and swelling of rubber in organic liquids. The manner in which small amounts of sulfur can produce such profound changes is not known with certainty, and it may act in several ways, but one way in which it appears to react is in forming sulfur bridges of some kind between the long rubber molecules. This causes the rubber to be elastic under stress,

rather than to flow, by making the permanent slipping of one molecule past another more difficult.

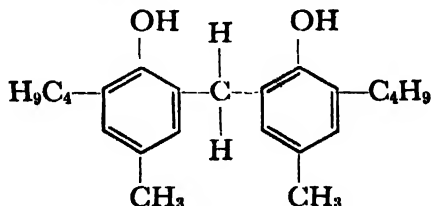
Vulcanization in the early days of the rubber industry required hours of time and rather large amounts of sulfur, around 8 per cent or more. As it is done now much less sulfur is needed and the time of vulcanization is a great deal shorter. The difference is caused by the use of substances known as *accelerators*, organic sulfur or nitrogen compounds which catalyze the vulcanization process so that it takes place faster and at lower tem-

peratures. This results in a better product because prolonged, high vulcanization temperatures tend to produce some deterioration of the rubber. Accelerators are added in small amounts, often less than one per cent. Some of them (the ultra-accelerators) cut the vulcanization time down to a matter of minutes, and the period of heating must then be carefully watched, to avoid over-curing.

Other Additives. Besides sulfur and accelerators, two other types of additives go into many rubber articles. One of these is the filler, a finely divided substance, often carbon, zinc oxide, or talc, which is added to improve the physical properties of the rubber. For example, addition of 25 per cent of carbon black will produce an increase in tensile strength of the resulting material of about 50 per cent.

The other additive is the antioxidant. This is commonly an organic hydroxide or a secondary amine (a compound containing the --NH-- group). Antioxidants added in small amounts inhibit air oxidation of rubber. In the early days of tire manufacture poor mileage resulted because the rubber in the tires combined with atmospheric oxygen and deteriorated to a product with insufficient resilience which quickly cracked and wore out. Then it was discovered that addition of these antioxidants in small quantities slowed up the onset of oxidation, and tires today have a much longer life because of this discovery.

The better antioxidants suffered for many years from the disadvantage that they discolored upon aging. This problem very recently appears to have been solved by use of compounds of the type shown below—good antioxidants which do not discolor with age.²



² The groups ortho and para to the hydroxyls are thought to prevent formation of chromophores (page 524) at those positions.

In summary, then, crude rubber is made into a useful product by milling it to produce plasticity; incorporating sulfur, accelerator, filler, and antioxidant; shaping it as in a mold; heating to vulcanize it.

Latex Rubber. A considerable quantity of latex is shipped as such, after it has been concentrated and stabilized. This increases shipping costs, since much water is shipped with the latex that is absent in crude rubber shipments. But rubber articles can then be made from the latex without first separating the rubber, hence the cost of separation, and also of milling, is saved. The same operations otherwise go on, i.e., addition of various materials and vulcanization, but they are performed on the latex instead of on crude rubber.

Latex rubber articles are shaped by dipping forms into the properly treated latex mixture, or by use of an electric current (electrodeposition), since the rubber and other particles present are charged, hence can be attracted to a form which has been made an electrode. The latex mixture can also be extruded in the form of rubber threads. These are used with other fibers to make products such as Lastex. The reader is familiar with latex rubber articles such as rubber gloves, toy balloons, bathing caps, etc. Latex rubber is superior to the milled product in that it is stronger and more extendible. It also has excellent resistance to aging, because of natural antioxidants present in the latex.

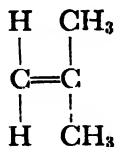
Sponge rubber articles are made in part by curing latex which has been whipped up to a foam with air. Carbon dioxide gas is also used. Bubbles of this are obtained by adding an oil suspension of sodium bicarbonate before curing. Other substances are also used to furnish gas bubbles

SYNTHETIC RUBBER

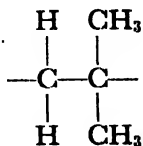
The modern chemist has been able to fashion a number of different kinds of molecules which in varying degree have the properties of rubber; these go under the general heading of

synthetic rubbers. The molecules in natural rubber are long and flexible, and with sufficient cross linkages between them to produce elasticity, but not so many as to cause rigidity. After much research the chemist has been able to make substances out of other long flexible molecules which make satisfactory and even superior substitutes for the natural product. If by rubber we mean a polymer of the C_5H_8 building unit, then the term "synthetic rubber" for these substitutes is incorrect, since none of them has the same building unit. However, public usage requires acceptance of the term. Synthetic rubber research has been greatly accelerated by the need for rubber, in Germany during the first world war and in many countries, including our own, in the second.

General Nature of Synthesis. The history and chemical details of synthetic rubber manufacture lie beyond the scope of this book, but in brief, synthetic rubber and other polymer molecules are made from relatively small molecules which are able to rearrange their structures so as to become building units. Many of the latter then combine in long chains to form rubber-like polymers. It is not possible for every small molecule to rearrange its electronic structure in this way. Molecules which do so commonly have one or more double bonds. Consider, for example, the substance isobutylene. It has the structure:

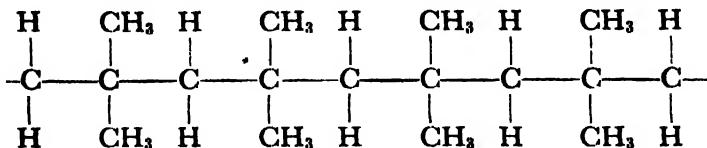


Under certain conditions, as in the presence of anhydrous aluminum chloride catalyst, isobutylene can be thought of, for simplicity, as rearranging to a building unit with two free valences.



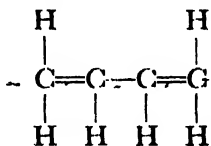
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Some hundreds or thousands of these units then combine to form long molecules of polyisobutylene, also known as polybutene. A portion of such a structure is shown below.

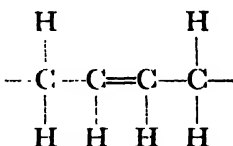


This is the main polymeric substance present in the butyl rubber³ which is now so popular in tire inner tubes, because of its air-retaining ability.

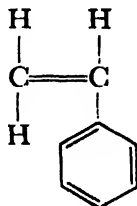
GR-S Rubber. The GR-S or Buna S rubber which has been our chief synthetic product for some years has chains consisting of two building units (copolymerization). One is butadiene.



which forms the building unit

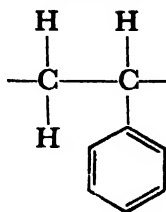


The other is styrene,



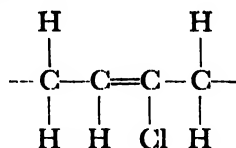
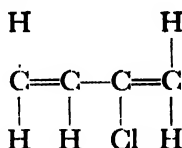
³ The other ingredient is isoprene (C_5H_8) which introduces double bonds so that the polymer can be vulcanized.

which rearranges to the building unit



These two together give a synthetic rubber consisting of long molecules which contain both building units. GR-S rubber is vulcanized with sulfur and accelerators, like 'natural rubber. It has found wide use in tires. In the last few years it has been found possible to polymerize this synthetic at low temperatures (cold rubber) to form a product which on tire treads gives higher mileage than can be obtained with either natural rubber or with ordinary GR-S rubber.

Other Synthetic Rubbers. Another valuable synthetic rubber is neoprene, which contains chlorine. The starting molecule, chloroprene, and its building unit form are shown below.



This rubber is often vulcanized with zinc oxide. Zinc chloride splits out and oxygen bridges form between rubber molecules. Neoprene has greater resistance to organic solvents than natural rubber.

Another synthetic product with high abrasion resistance is *Thiokol*. It has sulfur as well as carbon atoms in its molecules. *Nitrile* rubber contains carbon, hydrogen, and nitrogen. *Hycar* PA is a polyacrylic ester which can be used up to 400°F.

Rubber Production. It appears at this writing that synthetic rubber will be made eventually, and probably soon, which will be superior to natural rubber in all respects, and if cost is not too high the demand for natural rubber, like that for silk, may well

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decline as a result, to the further detriment of the Far East. At this writing natural rubber has increased in price to the point where synthetic rubber production is being stimulated.

TABLE 21.1 U. S. Production and Consumption of Rubber, Long Tons

<i>Type</i>	<i>Production</i>	<i>Consumption</i>
NATURAL	None	714,279
GR-S	358,048	412,578
RECLAIMED	313,381	302,631
BUTYL	55,832	66,237
NEOPRENE	50,067	42,472
N-TYPES	12,037	10,720

Self Study Questions

1. What is the etymology of the word rubber? Of caoutchouc?
2. Describe the occurrence and composition of latex.
3. What are the steps involved in making a rubber article from crude rubber? From rubber latex?
4. What is the building unit in the rubber molecule? Calculate the molecular weight of a rubber molecule containing 5000 of these building units.
5. How are the molecules arranged in unstretched rubber? In stretched rubber? What is the evidence on this point? How can we explain the return to its original shape of stretched rubber?
6. What changes in physical properties of rubber are produced by vulcanization? How do we explain the changes in terms of molecular structure?
7. From the difference in properties, what difference in molecular structure would you expect between ordinary vulcanized rubber and hard rubber (ebonite)?
8. Explain why accelerators, fillers, and antioxidants are used in the manufacture of rubber articles.
9. What general type of molecular change takes place in the making of synthetic rubber? Illustrate with polyisobutylene.

10. Would you think the substance isopentane, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2$, would make a satisfactory building unit for a synthetic rubber? Explain your answer.

11. Describe the chemistry involved in the making of GR-S rubber, as far as you have had it. What is a copolymer? How is GR-S rubber vulcanized?

12. What is the building unit in Neoprene rubber? How is this product vulcanized? In what way is Neoprene rubber superior to natural rubber?

13. Suggest a building unit (monomer), different from those in the book, from which a synthetic rubber polymer might be constructed. How would you vulcanize it?

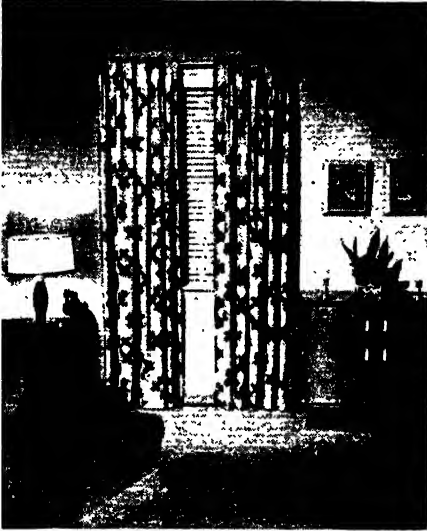
XXII

Plastics

Scope. The word plastic, from the Greek *plastikos* (to shape or mold), means different things upon different occasions. A surgeon may think of it as a type of surgery. To a scientist, it is a substance which will flow like a liquid under a high deforming force but not under a low one. Putty, wet clay, and paint are plastics under this definition. Likewise, under conditions of sufficiently high pressure, many solids not ordinarily considered to be plastic, and perhaps all solids, can be made to flow. But the general public does not think of these things as plastics.

To the average person a plastic is a hard, lustrous object, made of organic chemicals and therefore not able to stand high heat, able to be in contact with water and with the aqueous suspensions and solutions found in the home, but sometimes dissolved or injured by organic liquids. It may be transparent, translucent, or opaque, and often comes in bright colors. It has been formed in some way to give it a useful or decorative shape. This is the popular conception of the word plastic. The popular and scientific definitions can be distinguished from each other by using plastic as a noun for the former and as an adjective, i.e., plastic *substance*, for the latter. The chemistry of the popular type of plastic will be briefly discussed in this chapter.

The manufacture of plastics has become a major industry in the United States. The relatively low cost of manufacture, eye appeal, properties such as lightness and strength, all contribute to the saleability of these products, and plastic manufacturing has come up from its beginning in 1869 to a present level of many hundreds of millions of pounds annually. There is some



(a)



(b)

FIGURE 22.1. Chemicals to Furnishings. Plastic drapes, of the kind shown in (a), are made from vinyl plastics like that shown in the preblender in (b). Courtesy Union Carbide and Carbon Corporation.

uncertainty as to the present national output of plastics, since it depends upon what substances are called plastics. If materials such as rayon and the synthetic resins used in protective coatings are included, then the yearly output in this country is in the billions of pounds.

Many plastics, such as polystyrene and phenol formaldehyde, are synthesized from relatively small molecules in a process somewhat like that used in making synthetic rubber, i.e., the combination of many small molecules to form giant polymer molecules, with or without the splitting out of water. In polymers of this type the giant molecules become so large, or develop so many cross linkages, that elasticity of the degree possessed by rubber is not possible. Not all plastics are made from small starting molecules, however. Some, like the casein or cellulose plastics, start with natural products of high molecular weight.

Types of Plastics. Plastics can be divided into two broad, general classes, based upon their behaviour when heated. One

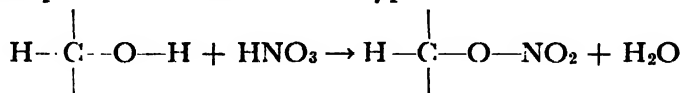
class of plastics softens sufficiently to flow when heated, and in this condition it can be molded or extruded to give desired shapes. These substances are the *thermoplastics*. The other class of plastics undergoes chemical changes upon the application of heat so that larger molecules and many cross linkages are formed. These substances, originally able to be molded, set and become rigid when heated. They are therefore called the *thermosetting* plastics. Each class is discussed below.

Synthetic Resins. It should be emphasized in connection with these materials that plastics are not pure chemical substances, any more than a rubber article, with its fillers, antioxidants, etc., is a pure substance. The major components are the *synthetic resins*, the giant organic molecules which determine the thermoplastic or thermosetting nature of the plastic, but even these are not pure substances, since they are made up of various-sized, although similar, molecules. In addition, fillers, plasticizers, pigments, and polymerization catalysts may be present. In most plastics there is a random arrangement of the component molecules so that the products are amorphous rather than crystalline.

THERMOPLASTICS

This type of plastic consists chiefly of polymer molecules long in one direction (linear polymers). They may be from naturally occurring material, like cellulose, or they may be built up from small units. One of each type will be considered.

Cellulose Nitrate. Plastics based upon this substance were the first to be manufactured in the United States (1869), and are still made, but in diminishing amount. An early use was in the celluloid collar of those days. If the reader will refer to the carbohydrate building unit which is the basis for the cellulose molecule (page 366), he will see that it contains three hydroxyl groups. Theoretically all three of these can be replaced by nitrate groups in a reaction of the type:

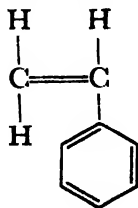


If this complete nitration took place in each building unit in a giant cellulose molecule, a product containing 14.15 per cent nitrogen should result. A nitrogen content this high is not obtained in any industrial nitration of cellulose, although a value of nearly 14 per cent is reached in the manufacture of smokeless powder. In the product used for plastics the nitrogen content is kept down to around 11 per cent. The giant cellulose molecules are also broken down in the process to smaller parts containing about 500 carbohydrate building units. It is necessary to add sulfuric acid in the nitration to remove the water formed and prevent a back reaction.

The resulting product is too brittle to be molded, and by itself it is therefore not a plastic. But when it is mixed with camphor and alcohol the mixture changes in character to one which can be shaped. Camphor and other substances used for this purpose in plastic manufacture are called *plasticizers*, since their function is to separate the giant synthetic resin molecules sufficiently so that rigid cross linkages do not form and destroy plasticity.

Cellulose nitrate suitable for plastics is called *pyroxylin*. It is at present made into molded articles and extruded to produce rods and tubes. The plastic has the advantage that it can be machined, and two surfaces can be joined by moistening each with acetone and sealing them together under pressure. Cellulose nitrate has also been employed in the past as a fiber and as the plastic layer in safety glass, but these uses have now largely been discontinued, the first because of the cost and the second because cellulose nitrate is not sufficiently light stable in thin sheets. The material also has the disadvantage that it is highly flammable.

Polystyrene. The substance styrene is ethylene (page 337) with one hydrogen substituted by a benzene ring (C_6H_5-).



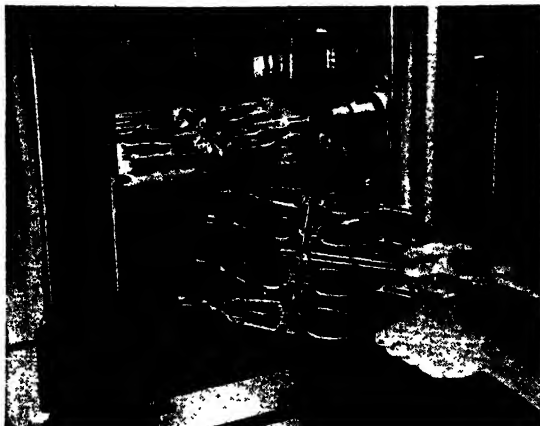
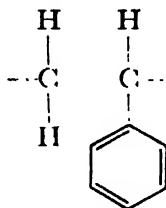
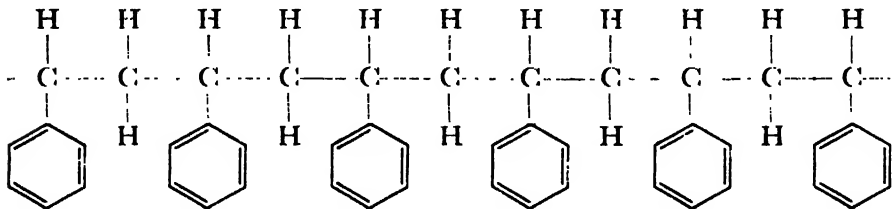


FIGURE 22.2. Polystyrene Plastic. Courtesy Union Carbide & Carbon Corporation.

It is prepared by heating a mixture of benzene and ethylene. Under the influence of light, heat, oxygen, or oxidizing agents styrene can be thought of as undergoing a bond rearrangement to form the building unit shown below.



Linear polymers then form containing hundreds or thousands of these units, probably linked head to tail.



Polystyrene is commonly made into plastic articles by injection molding in which the heated, fluid plastic is forced under pressure into molds. It is characterized by unusual clarity.



(a)



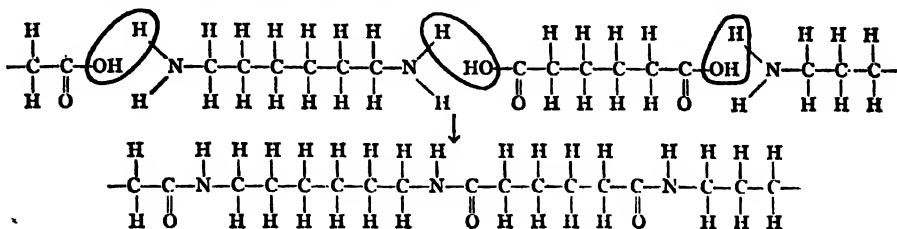
(b)



(c)

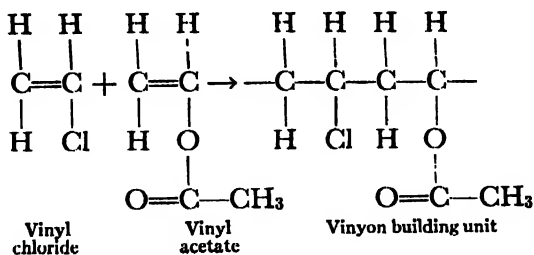
FIGURE 22.4. Nylon Manufacture. (a) Nylon polymer is formed in these large pressure cookers, known as autoclaves. (b) The polymer is extruded through spinneret holes. (c) The filaments are wound together to form Nylon yarn, shown here being checked for density. Courtesy E. I. du Pont de Nemours & Co.

When these compounds are heated under pressure they combine, with the splitting out of water, to make giant linear polymers containing alternate building units from the acid and the amine.

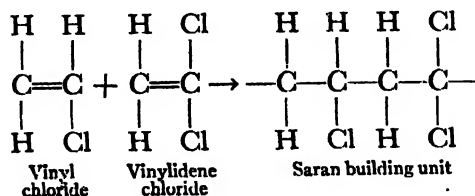


Sebacic acid, with a molecule four carbon atoms longer than adipic acid, is also used, in place of adipic acid, in making Nylon. The molten material is extruded through fine holes as threads which solidify in this form in an inert atmosphere of nitrogen. The solid threads are then stretched to about four times their original length to pull the molecules into more nearly parallel positions, causing greater tensile strength, transparency, and luster. Nylon is also made into larger filaments (monofilaments), used for bristles and tennis racquet strings, and into still larger objects, such as gears, bearings, and soft-impact hammers.

Two other important synthetic fibers are Vinyon, made from vinyl chloride and vinyl acetate,



and Saran, from vinyl chloride and vinylidene chloride.



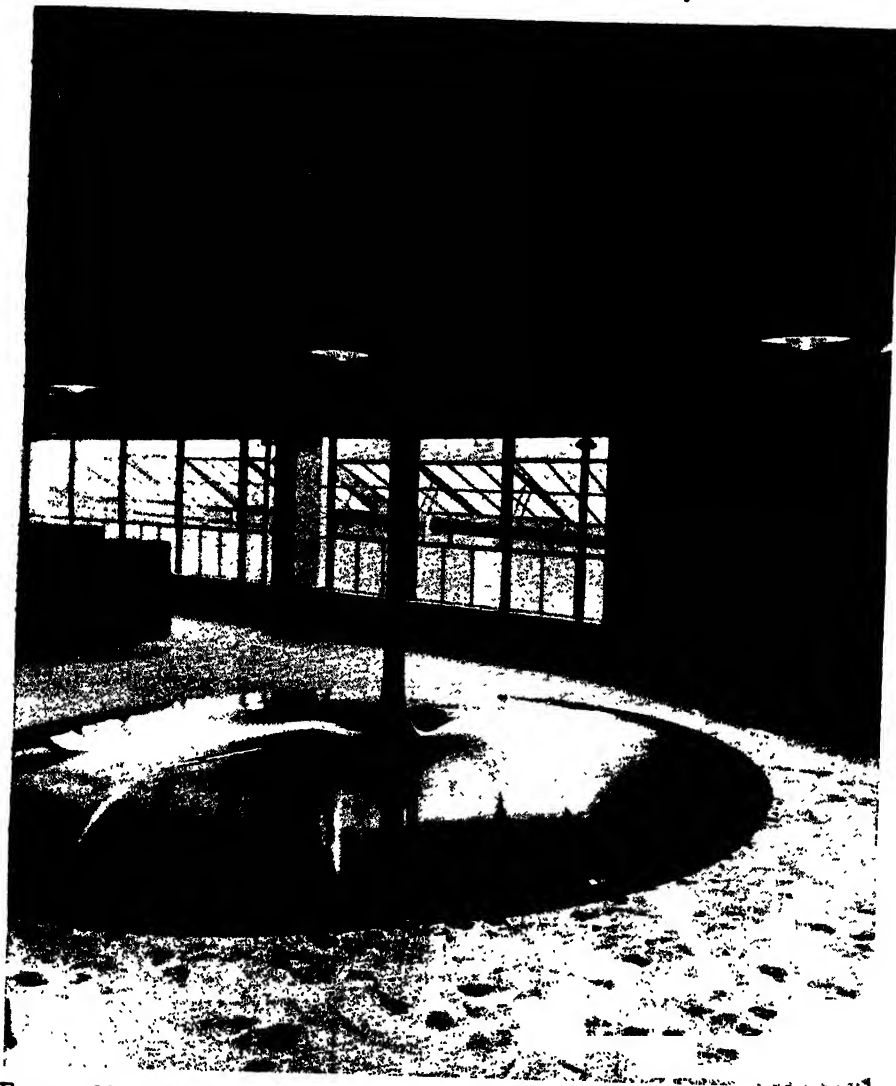


FIGURE 22.5. Thermosetting Resin Formation. In this initial stage, phenol-formaldehyde resin, thermoplastic during its first heating, is poured on the cooling floor. After solidification this is ground and mixed with other ingredients. Thermosetting plastic articles are made by heating the resulting powder in molds. Courtesy Monsanto Chemical Company.

Orlon is a synthetic fiber in which the building unit is ethylene with one hydrogen replaced with a $-\text{CN}$ group. Dynel is a copolymer of this with vinyl chloride. Dacron is a condensation

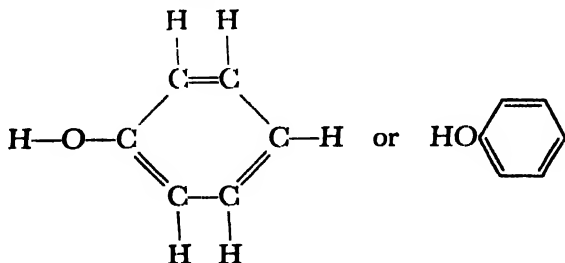
polymer of ethylene glycol with dimethyl terephthalate. Vicara is a zein fiber, made from corn protein. Some of these synthetic fibers suffer from the disadvantage that they are injured by dry cleaning fluids.

Another group of fibers of great importance are those made from cellulose and casein, i.e., cellulose and cellulose acetate (rayon), and formaldehyde-hardened casein. These fibers are only semisynthetic, however, because the giant molecules present are from natural sources.

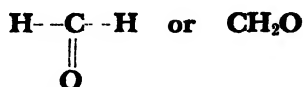
THERMOSETTING PLASTICS

Thermosetting plastics consist chiefly of giant three-dimensional molecules which decompose, rather than melt, when heated. In the manufacture of thermosetting plastics advantage is taken of the fact that time is necessary for the formation of the large, infusible molecules which are present in the final product. Since the process is not instantaneous, it is possible to stop it at a stage considerably short of completion, by merely lowering the temperature of the reaction mixture. At this stage the polymerization has produced only relatively small molecules which melt and which are thermoplastic. The cold, solidified material can be ground and mixed with fillers, pigments, etc., and the resulting powder (molding compound) can then be placed in a mold and heated further under high pressure (compression molding). The reaction then proceeds to the final stage, and the thermosetting plastic is formed.

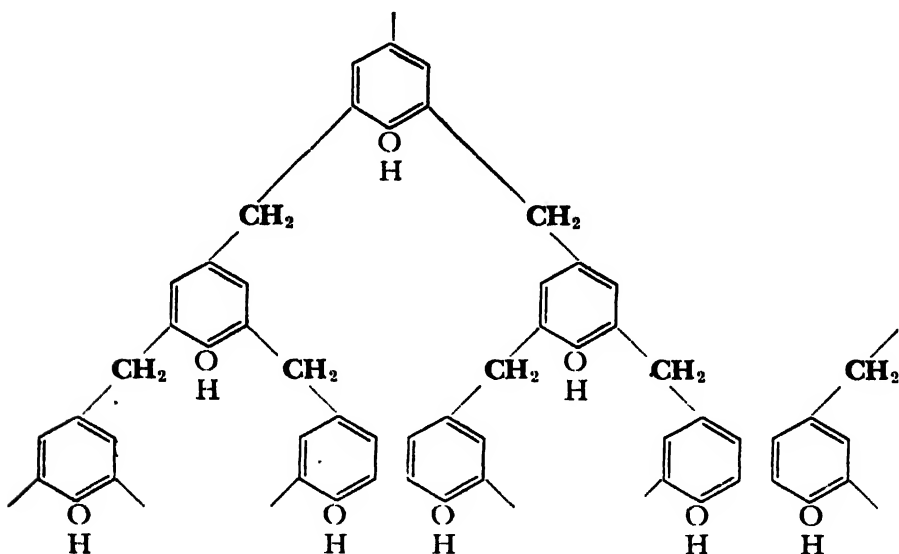
One important plastic of this type contains polymer molecules made from phenol and formaldehyde (condensation polymerization). Phenol is hydroxybenzene.



Formaldehyde is the simplest organic compound containing carbon, hydrogen, and oxygen.



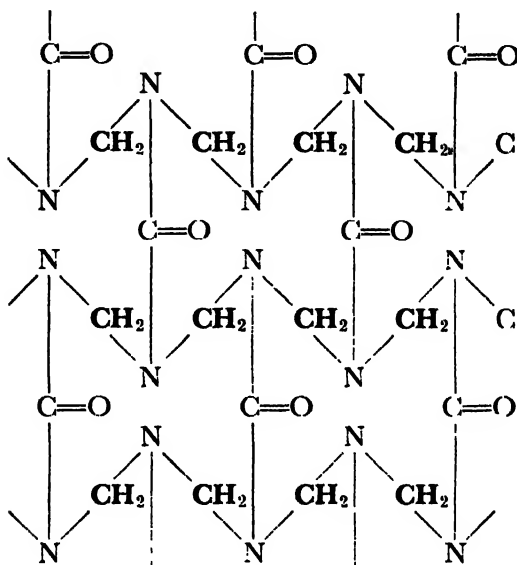
When phenol and formaldehyde are heated together the ortho and para¹ hydrogen atoms on the benzene ring form water with oxygen atoms from formaldehyde, and a structure like that shown below results. This is only a small portion of the entire giant molecule.



The reader is familiar with phenol formaldehyde plastics under the trade name of "Bakelite," and many of the dark colored plastic objects in the home used in telephones, small radio cabinets, buttons, electrical parts, etc., are of this type. The Bakelite patents expired in 1926, and several dozen companies are now making phenol formaldehyde and related plastics. The Bakelite Company also makes other types of plastics under this name.

¹ See page 343 for the meaning of ortho and para.

Another important type of thermosetting plastic is that based upon urea-formaldehyde resin. Urea, $\text{CO}(\text{NH}_2)_2$, reacts with formaldehyde, with the splitting out of water, to form a giant molecule with the structure shown partially below.



Plastics made from this resin are sold under such names as Plaskon and Beetle. They have a wide variety of uses, as in lighting appliances, buttons, toys, piano keys, tableware, dials, and handles, etc.

The molded types of plastic such as those just described may contain a third, or even more, of materials other than the synthetic resin. Finely divided wood (wood flour) is often present as a filler and the giant resin molecules can then be thought of as binding the filler particles together in the final plastic article. Synthetic resins are used as bonding agents in other products besides plastics. They are employed in some adhesives. They form the bond in such things as plywood and safety glass, and in some protective coatings, where they bind the pigment particles together and to the painted surface.

Plastic production in the United States for 1947 follows:

<i>Type</i>	<i>Pounds produced</i>
CELLULOSE (nitrate, acetate, esters)	90,331,982
PHENOLIC AND RELATED RESINS	319,040,398
UREA AND MELAMINE RESINS	74,291,587
POLYSTYRENE	94,990,618
VINYL RESINS	183,837,465
OTHERS	85,978,117

S U M M A R Y

Plastics, according to the popular conception of the term, are fairly hard, lustrous, shaped articles. They contain as the main component various types of giant organic molecules (synthetic resins) and as lesser components fillers, plasticizers, pigments, and polymerization catalysts. If the giant organic molecules making up the resins are long in one dimension, and without many cross linkages, the plastics can usually be softened by heat to the point where they can be shaped by injection molding, rolling, or extrusion. This type of product is known as a thermoplastic. If the resin molecules are large in three dimensions the plastic is of the thermosetting type. In this case polymerization is stopped at an intermediate stage and the resin is ground and mixed with other materials, then formed into desired shapes and heated, whereupon the polymerization completes itself, giving a product which does not soften at elevated temperatures, although it can be decomposed into simpler molecules.

Examples of thermoplastics are regenerated cellulose and its esters, vinyl plastics, including polystyrene, and acrylic, casein and polyethylene plastics. Examples of thermosetting plastics are phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, polyesters, and alkyd plastics.

When thermoplastics are extruded in filament form for use in textiles they are called synthetic fibers. These have a less random arrangement of molecules than ordinary plastics. The linear polymer molecules present in these fibers are oriented during extrusion and by stretching so that their long axis tends to coincide with the long axis of the fiber.

Self Study Questions

1. How does the scientist's conception of a plastic substance differ from the popular conception of a plastic?
2. What is a thermoplastic substance? What type of giant molecule characterizes these?
3. Show by an equation what happens when nitric acid acts upon the carbohydrate building unit $C_6H_{10}O_5$. Is nitration complete in the manufacture of pyroxylin?
4. Is cellulose nitrate by itself a plastic substance? How is it made into a plastic? What are such addition agents called?
5. Write the structural formula for styrene. How does the bonding change when polystyrene is formed? How are plastic articles made from polystyrene?
6. What is a synthetic fiber? How do these differ from ordinary plastic articles made from the same synthetic resin?
7. What two substances react to form Nylon? How are Nylon filaments prepared? What is the purpose of the last stretching operation?
8. How many adipic acid and hexamethylene diamine molecules would be required to make a Nylon polymer molecule with a molecular weight of 226,326? *Answer: 1000 of each.*
9. Name several other synthetic fibers and describe the molecules from which they are made.
10. How does the resin in a thermosetting plastic differ in molecular shape from thermoplastic resins?
11. Polymerization is made to take place in two stages in the manufacture of thermosetting plastics. Explain why it is done in this way.
12. What type of molecular structure results when phenol and formaldehyde react? Write the formula for the simplest possible reaction product between these two substances.
13. Distinguish between a plastic and a synthetic resin. What substances may be present in a plastic besides the synthetic resin?
14. Name at least a dozen articles in your home made from plastics.
15. How else are synthetic resins used besides in plastics?

XXIII

Paint and Similar Coatings

Paints, enamels, varnishes, and lacquers, used for protection and decoration, can be thought of in one sense as adhesives applied to a single surface only, and indeed, substances used in adhesives may also be present in protective coatings, as cellulose nitrate or phenol formaldehyde resins. Both must have adhesion to the surface to which they are applied and cohesion within the film. To the average person the word "paint" may include all types of protective or decorative coatings applied by dipping, spraying, or with a brush, but the technical man in this field recognizes distinctive differences between paints, enamels, varnishes, and lacquers, with some hard-to-classify borderline products, however. Each of these four types of coatings is described briefly in this chapter.



FIGURE 23.1. Paint Pigment Dispersion. A roller mill is used to disperse zinc oxide. Courtesy American Zinc Institute.

PAINT

Composition. Paint is a semifluid product consisting of a finely divided pigment suspended in a liquid known as a vehicle, together with small amounts of other substances added for

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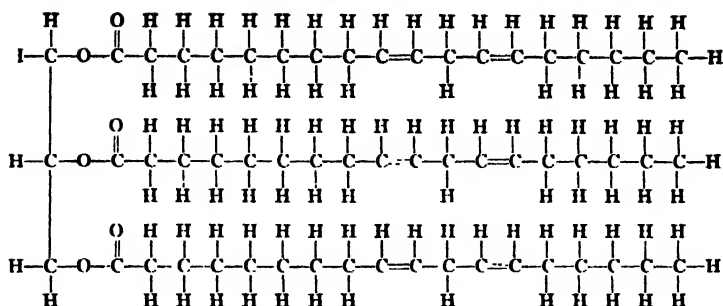
special purposes. The vehicle, particularly in exterior paint, is a mixture of drying oil, such as linseed oil, and thinner, such as turpentine. After application of the paint the thinner evaporates, and the drying oil changes chemically to a solid, somewhat pliable film which binds the pigment particles together and causes the paint to adhere to the surface which it protects.

Paint Pigments. The pigment may be of any color, and a great variety of substances are used for this purpose. A few common paint pigments are listed in Table 23.1.

TABLE 23.1 Important Paint Pigments

<i>Name</i>	<i>Chemical composition</i>	<i>Color</i>
ZINC OXIDE	ZnO	White
ZINC SULFIDE	ZnS	"
LITHOPONE	ZnS and BaSO ₄	"
BASIC CARBONATE WHITE		
LEAD	Pb(CO ₃ , OH)	"
BASIC SULFATE WHITE		
LEAD	Pb(SO ₄ , OH)	"
TITANIUM DIOXIDE	TiO ₂	"
OCHRE	Clay plus iron oxide	Yellow
CHROME YELLOW	Normal or basic lead chromate	"
VENETIAN RED	Fe ₂ O ₃	Red
INDIAN RED	Fe ₂ O ₃	Bluish-red
RAW SIENNA	Clay plus iron oxide	Brownish-yellow
BURNT SIENNA	Clay plus iron oxide	Reddish-brown
PHTHALOCYANINE BLUE	Copper phthalocyanine	Blue
IRON BLUE	KFe(Fe(CN) ₆)	Blue
CHROME OXIDE GREEN	Cr ₂ O ₃	Green
CARBON BLACK	Carbon from natural gas	Black
LAMPBLACK	Carbon from tar or mineral oil	"
<i>Extender pigments</i>		
CHALK	CaCO ₃	White
BARYTES	BaSO ₄	"
TALC	Magnesium silicate	"
CHINA CLAY	Aluminum silicate	"
MICA	Complex silicate	"

Drying Oil. The drying oils used in paints are mixed glyceryl esters of (mostly) unsaturated acids (page 386). The linoleate radical is prominent in these oils. Pure glyceryl linoleate has the structure shown below.



Linseed oil is the chief drying oil used. The raw oil is slow to dry, and to quicken the process it is often heated and air passed through it before it is employed in paint. This produces a

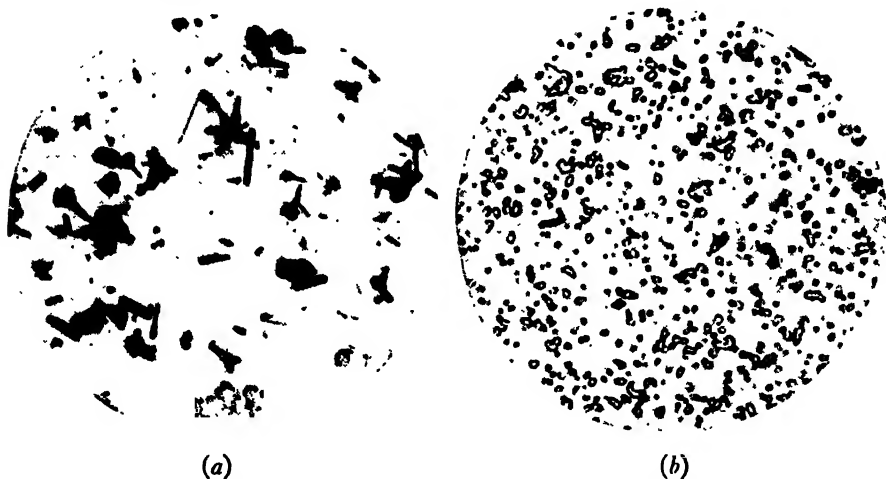


FIGURE 23.2. Paint Pigments. (a) Zinc oxide particles, enlarged 5000 times. (b) Orange chrome yellow particles, enlarged 1000 times. This substance is basic lead chromate. Courtesy National Paint, Varnish and Lacquer Association.

preliminary polymerization, giving a product with a higher viscosity which “dries” more quickly after the paint has been applied. Metallic salts of organic acids are also added in small amounts as catalysts to speed up the drying process.

The actual drying mechanism is not thoroughly understood. Oxygen is taken up, and cross linkages are formed between ester molecules, undoubtedly at the double bonds. The process may be somewhat like that which takes place during the vulcani-

zation of rubber. The cross linkages may involve oxygen bridges, or perhaps oxygen acts only catalytically and the linkage is between carbon atoms. The drying is in part an actual drying, since any thinner present in the paint evaporates. But this leads only to a more viscous but still fluid paint, and polymerization and oxygen absorption are necessary before a solid paint film results.

Other Paint Components. Besides *drying oil*, *thinner*, and *pigment*, other substances may be present in a paint. Another solid component, the *extender*, is frequently added. Extenders serve several useful purposes. In some cases they help to make a more resistant paint film, particularly when they consist of plate-like particles which orient themselves parallel with the surface. They may increase the plasticity of the paint (see below). They sometimes prevent the “hard” settling of a pigment, causing instead a “soft” settled layer which easily mixes up when the paint is stirred. Extenders are usually relatively coarse white substances such as calcium carbonate or magnesium silicate, which can be used even in the presence of colored pigments. The color is not significantly diluted with addition of ten or twenty per cent of extender, because the particles of the latter are coarser than those of the pigment and are coated with the pigment particles.

Driers will also commonly be present. Their use was mentioned earlier. Lead, cobalt, and manganese naphthenates are often employed for this purpose. Other substances sometimes added in small amounts are *antiskinning agents*, to prevent film formation in the can. They are organic compounds which often contain nitrogen. If antiskinning agents can be made effective enough in the future perhaps paint manufacturers can start selling their products in larger, only partly filled cans. This will be a welcome change to millions of paint users who are now faced with the somewhat messy task of either stirring a completely filled can of paint or of pouring it partly into another container before stirring and thoroughly remixing.

Manufacture of Paint. The pigment is finely dispersed in a portion of the vehicle, not only to give a smoother paint film, but also to increase the covering power. Various types of equipment are used for this purpose. Buhrstone mills consist of large, flat stones which turn as the pigment passes between them. Pebble and ball mills are rotating cylindrical containers having in them pebbles or steel balls and the pigment to be ground. Collisions between the pebbles or balls break up pigment aggregates which happen to lie between them. In roller mills the pigment is passed between pairs of rolls, one of which is rotating faster than the other, causing a shearing action. These various devices are thought not to do much actual grinding but to break down groups of pigment particles into smaller groups, or into individual particles. Some liquid is present during the grinding, but more must be added later to make the final paint.

Not all pigment agglomerates need be dispersed by mechanical action of this kind. When white lead pulp (the pigment wet with water), for example, is mixed with linseed oil, the water gradually separates and the pigment disperses itself in the oil. Many other dispersions are similarly made, in a process known as *flushing*.

Plasticity of Paint. Paint behaves differently from a true liquid in the manner in which it flows. This is chiefly due to the pigment present, since the oil itself does not show such behaviour. In Figure 23.3 is given the rate of flow of paint, and of the oil in paint, as the pressure (or other force) causing the flow is changed. The oil itself is seen to behave like a true liquid, i.e., its flow curve is a straight line passing through the origin. But the paint does not flow at all until a certain minimum force is applied, called A in the drawing. This type of flow is known as *plastic* flow. The reader is familiar with substances in the home which exhibit plastic flow. A piece of butter, for example, retains its shape in a dish. The force of gravity is not sufficient to cause it to spread out like a liquid, at ordinary temperatures. But if a sufficient force, greater than gravity, is applied, the butter can

be made to change shape like a viscous liquid. Paint behaves in this manner, but not as obviously so as butter, because it flows under a much smaller deforming force.

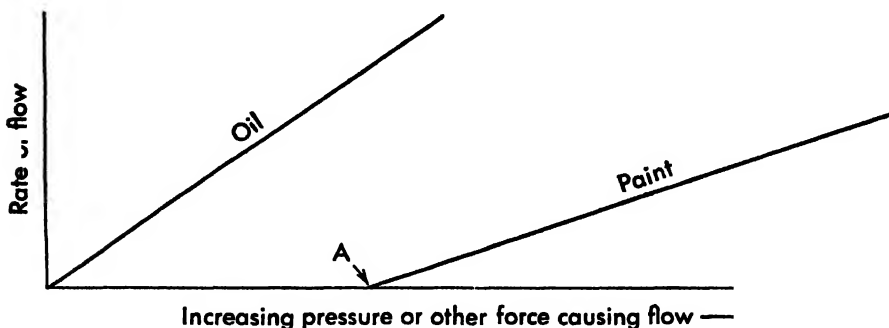


FIGURE 23.3 Difference in Type of Flow between Oil and Paint.

It is desirable that paint exhibit plastic flow, particularly in the coating of vertical surfaces, since otherwise it would tend to flow under the influence of gravity and form “curtains” during the painting of walls, fences, etc.

ENAMEL

To the expert an enamel differs from an exterior paint in that it forms a smoother, harder and usually glossier film. Not all enamels are more glossy than paint, however, and “semigloss” enamels are common and popular. The hiding power, in the glossy range, is lower than that of paints, because of a smaller pigment content. Imperfections in an underlying surface are more poorly hidden by an enamel, but on the other hand brush marks tend more readily to disappear. Both of these differences are due to the fact that enamels flow more readily than paints, hence cannot be applied as thickly. There is no sharp dividing line between paint and enamel, and many gradations exist.

Enamels differ from exterior paints in composition in that a varnish is present in the former but not usually in the latter. A brief discussion of the chemistry of varnishes follows.

VARNISH

A varnish is a protective coating without pigment, consisting of a film-forming material (a resin), a volatile solvent for this, and perhaps a drying oil. If the latter is present the product is

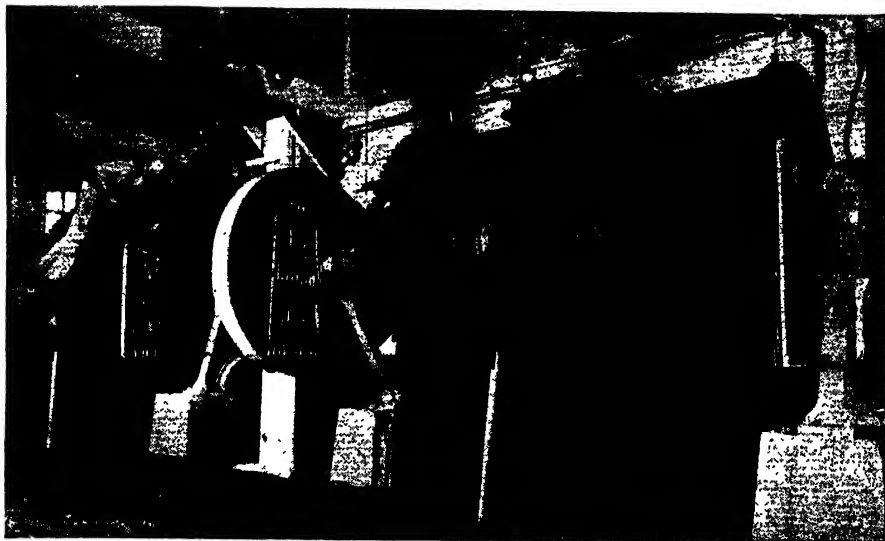
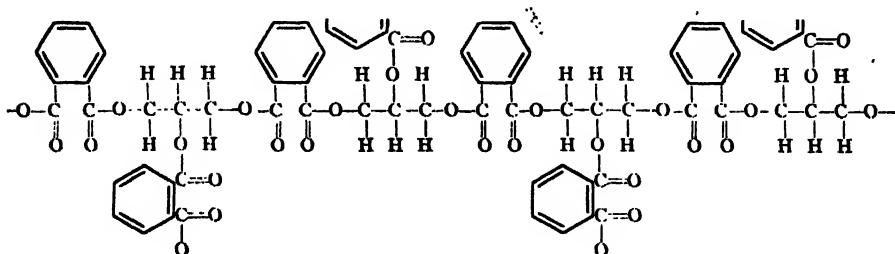


FIGURE 23.4. Ball Mills. The ones shown have a capacity of 500 gallons. They are used for dispersing paint pigments. Courtesy The Sherwin-Williams Co.

known as an *oil* varnish, if absent it is a *spirit* varnish. Varnishes are used, both by themselves and in other coatings, such as enamels.

Oil Varnish. Oil varnishes are solutions, in a volatile organic solvent, of a mixture of resins and drying oils. The two film formers are heated together first, before addition of the solvent. If the resin is a synthetic it is often prepared in the presence of the oil, and the two are thought to combine chemically. After application of the oil varnish the film-forming process is even more complicated than in the case of drying oils alone, because it is partly a drying oil oxidation and polymerization and partly the evaporation of the synthetic resin suspension which produces this film.

Among the synthetics not previously mentioned used in the manufacture of varnishes are modified *alkyd* resins. They are formed as condensation polymers when phthalic anhydride and glycerine react in the presence of drying oils or others. The structures of the modified alkyd resins are not known with certainty, but a section of an unmodified alkyd resin molecule is shown below.



This unmodified molecule is not sufficiently soluble in paint and varnish liquids, hence the alkyds used in protective coatings are always modified by heating with oils during their preparation. Other synthetic resins are also employed in varnishes, such as *phenol formaldehyde*, *urea formaldehyde*, *vinyl resins*, etc. Natural resins, the exudate from various trees, such as the dammars or copals, may also be employed.

Some varnishes and enamels are baked to give a superior film, and in fact most oil varnish finishes are improved by baking.

Spirit Varnish. Spirit varnishes contain no drying oil; hence, they are chemically simpler than oil varnishes. They are a solution of a natural or a synthetic resin (or both) in a volatile solvent. Some natural resins must first be heated, to bring about a partial decomposition, before they become sufficiently soluble to use in spirit varnishes. Natural resins, some of which are less expensive than the synthetics, can sometimes replace a considerable amount of the latter without causing a great change in the quality of the varnish.

Earlier spirit varnishes employed alcohol as a solvent, as for example a manila resin solution in that liquid. Later, alcohol-

benzene and alcohol-hydrocarbon mixtures were used, since these dissolved a greater number of resins, including synthetics. Plasticizers, such as tricresyl phosphate, were then incorporated to improve the nature of the film and to permit use of harder, cheaper resins.

LACQUERS

The word lacquer originally meant a spirit varnish, and particularly one containing either the substance shellac (India, Burma), or the sap of the tree *Rhus vernicifera* (China, Japan). The art of applying this to wooden or metal surfaces, long practiced in the Far East, was known as lacquering. The meaning of the term has been retained as far as the mechanism of drying is concerned, but in this country, until recently, the term has been pretty much restricted to protective coatings containing cellulose derivatives, chiefly cellulose nitrate. However, today there is an increasing use of vinyl, synthetic rubber, and other polymers in lacquers.

It has long been known that cellulose nitrate could be dissolved in organic solvents and made into a protective film by permitting evaporation of the solvent. But early cellulose nitrate solutions were so viscous that they had to be made very dilute, giving thin films. These, furthermore, had rather poor adhesion, were brittle, and deteriorated when exposed to light.

Research has overcome most of these difficulties. Less viscous solutions are made possible by using the proper mixture of solvents, and by the proper preparation of cellulose nitrate itself. Brittleness has been remedied by using plasticizers, and adhesion and gloss have been improved by including other resins. The cellulose nitrate and resin are dissolved in the solvent, frequently an acetate ester of low molecular weight, such as ethyl or butyl acetate, and diluents, plasticizers, stabilizers, and pigments are then added. A lacquer is therefore a rather complex mixture.

Other cellulose esters are sometimes used in lacquers, usually cellulose acetate and mixed esters such as the acetate-butyrate.

Cellulose ethers, chiefly the ethyl ether, are also employed in the compounding of some lacquers.

Lacquers have the big advantage that the film dries rapidly, much faster than the drying oil type of protective coating. This has made lacquers popular in manufacturing operations where speed is important, as in the coating of automobile bodies.

OTHER COATINGS

Shellac is an alcoholic solution of the lac resin, a product formed by the lac insect. The word is thought to come from the Sanskrit "lakska," meaning hundred thousand, and undoubtedly referring to the vast numbers of these insects found on trees in various parts of India. The lac resin and also a deep red dye (lac dye) are formed as a secretion by the insect, and both are purified and sold. The solid lac is separated from the twigs where it accumulates by use of hot water. It is melted, strained, and recovered as flakes which are then called shellac. The alcohol solution used for coating is actually a spirit varnish; it is considered separately here because of its different name and the unique source of the resin.

Water is employed as the dispersion medium in a growing number of protective coatings. This has the advantage of cheapness and greater freedom from odors and fire hazards, but on the other hand not all film formers are as readily suspended in water as they are in organic solvents. The reader is probably familiar with the water paints used for art work. Other products are available in which water-dispersible organic film formers are employed, such as casein. In still others an emulsion is formed between an oil product in concentrated form and water. In this category are the interior oil (or resin) emulsion paints which are popular at present. They are largely ester gum varnish emulsions.

Classification of Protective Coatings. So many varieties of protective and decorative coatings exist that an all-inclusive, exact classification is difficult; one authority told the writer that

a four-dimensional diagram was required. Below, in Table 23.2, is a rough classification which includes most of the familiar coatings.

TABLE 23.2 Classification of Protective and Decorative Coatings

PROTECTIVE AND DECORATIVE COATINGS	{	Aqueous systems	{	Clear { Glue size
				Opaque { Cascin paint Calcimine Emulsion paint
	{	Nonaqueous systems	{	Clear { Spirit varnish Oil varnish
				Opaque { Enamel Lacquer Exterior paint

Self Study Questions

1. In what general ways do protective coatings resemble adhesives?
2. What components are present in exterior paint? What is the most widely used drying oil?
3. Give examples of some paint pigments. What element is used to make nearly all black pigments? Most brown pigments are due to what substance?
4. In what two ways is a drying oil treated to make it harden more rapidly after application of the paint?
5. What types of chemical changes take place when a drying oil film hardens?
6. How does paint differ from a true liquid in its flow characteristics? What is meant by plastic flow? Why is it an advantage for paint to have plastic flow?
7. How does an enamel differ from an exterior paint?
8. What is the function of a resin in a protective coating? Give some examples of natural and synthetic resins.
9. What processes are thought to take place during the drying of an enamel film?
10. Name two types of varnishes and distinguish between them.

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11. How has the meaning of the term lacquer changed with the times? What is the present meaning? What components are present in a lacquer?

12. What is shellac? What is the source of this resin?

13. Give examples of protective coatings in which water is used as a vehicle.

14. What would be the disadvantage of using as protective coatings (a) a mixture of iron oxide and water, (b) a mixture of turpentine and flour, (c) drying oil, thinner, drier, and finely divided sodium chloride as a pigment?

15. Construct a classification scheme for protective coatings.

XXIV

Cleaning Agents

TYPES OF CLEANING

The cleaning of surfaces is done (*a*) by chemical action, (*b*) mechanically, as with abrasives, (*c*) by a process of physical solution, (*d*) by the emulsifying or deflocculating action of soap and other detergents.

Cleaning by Chemical Action. Strictly chemical cleaning is not frequently employed in the home, although it is of some industrial importance, as in the pickling baths used for cleaning metals prior to coating them. What might be considered an example of chemical cleaning in the home is the cleaning of silverware by the use of the metal couple principle (page 242). Excess electrons accumulating upon the dark surface layer of silver sulfide are thought to cause the removal of sulfur as sulfide ions.

Cleaning by Physical Solution. Whenever water soluble "dirt" is removed with water this type of cleaning is being employed. Examples are the dissolving of syrup spots from cloth, the washing of candy residues from children's sticky hands, the removal of water-soluble dyes and inks with water. The dissolving of grease spots with carbon tetrachloride or other organic solvents ("dry" cleaning) is another example of this type of cleaning, as is also the removal of paint spots from hands or floor with turpentine. There are many other methods for the removal of spots and stains. A summary of these is given in Appendix G.

Mechanical Cleaning. Much of this goes on in the home, partly in connection with other types of cleaning, as in the rubbing action of a wash cloth or brush and the scrubbing of floors, where detergents are also being employed. Or, mechanical cleaning may be used by itself, as the action of a dust cloth or of an abrasive like steel wool. While there is no chemistry involved in strictly mechanical cleaning, the latter is often used to insure better contact between the dirt and one of the other types of cleaning agents.

Cleaning by Use of Detergents. Besides the three types of cleaning just described, there remains a highly important fourth type, in which particles of dirt are removed from a surface because they have a preference for an emulsifying or deflocculating agent added for the purpose of getting them into suspension. The dirt in question is largely unchanged in the process; hence, the action is not a chemical one, at least not to the extent of the chemical changes mentioned in the first type of cleaning. It is rather one of causing the impurity to be dispersed into small droplets, if it is a liquid (emulsification) or into small particles, if it is a solid (deflocculation). These droplets or particles leave the surface to which they were originally attached and form a colloidal dispersion in the liquid present (usually water). Substances which clean in this general way are known as *detergents*.

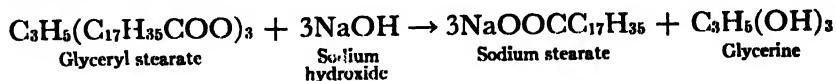
SOAP

Soap Manufacture. The commonest agent for emulsifying and deflocculating dirt is still soap, although competitive detergents are becoming increasingly popular. Soap is made by treating fats or fatty oils, such as tallow, lard oil, palm oil, olive oil, cocoanut oil, cottonseed oil, etc., with (generally) sodium hydroxide solution. These fats or fatty oils are glycerine esters of organic acids having fairly high molecular weights (page 384). In the reaction with sodium hydroxide, metal salts of the organic acids (soaps) are formed, together with glycerine. The process is known as *saponification*. Consider, for example, the saponification of beef



FIGURE 24.1 Soap Making. The traditional method of making soap in which fats and oils are boiled with alkali in large tanks called kettles. This photograph shows a section of the top floor of a modern kettle house. Courtesy The Procter & Gamble Company.

tallow. One of the components of this material is glyceryl stearate, or stearin, $\text{C}_3\text{H}_5(\text{C}_{17}\text{H}_{35}\text{COO})_3$. Using this to illustrate the chemical change:



Soap at one time was made in the home from fats and the alkaline substances in ashes. Today soap making has become an important industrial process. It is carried out in large, stainless steel containers, by heating fats or oils with sodium hydroxide solution. After completion of reactions like the one shown in the equation above the soap remains dispersed throughout the solution. It is flocculated, or brought together in one mass, by the addition of salt. The soap rises to the surface and is removed, then mixed with other ingredients, some of which, while improving color and odor, do not add to the cleaning ability. The final mixture is allowed to harden, following which it is cut into cakes. While soap is in general made in this manner, the descrip-



FIGURE 24.2 Soap Making. Interior of a soap kettle during saponification. Courtesy The Procter & Gamble Company.

tion just given is somewhat oversimplified, since some of the steps are more complicated than outlined.

Types of Soap. Many kinds of soap are manufactured, as the reader well knows, and some of the variables should be briefly considered. The hardness of a dry soap is determined by the molecular weight and degree of saturation of the fat, and by the water content. Some soft soaps are potassium soaps, made by action of potassium hydroxide upon fats.

Castile soap was originally formed by treating olive oil with sodium hydroxide. Products now sold under this name may be made in part from cocoanut, linseed, or cottonseed oils. *Floating soap* is obtained by agitating soap and blowing air into it until a product results which is lighter than water. *Salt water* or *marine soap* is made from cocoanut oil. Soaps from this source contain fewer carbon atoms per molecule than those made from tallow, and they are more soluble in salt water. They lather in either salt or fresh water. *Oil* (naphtha) *soaps* have hydrocarbon oils

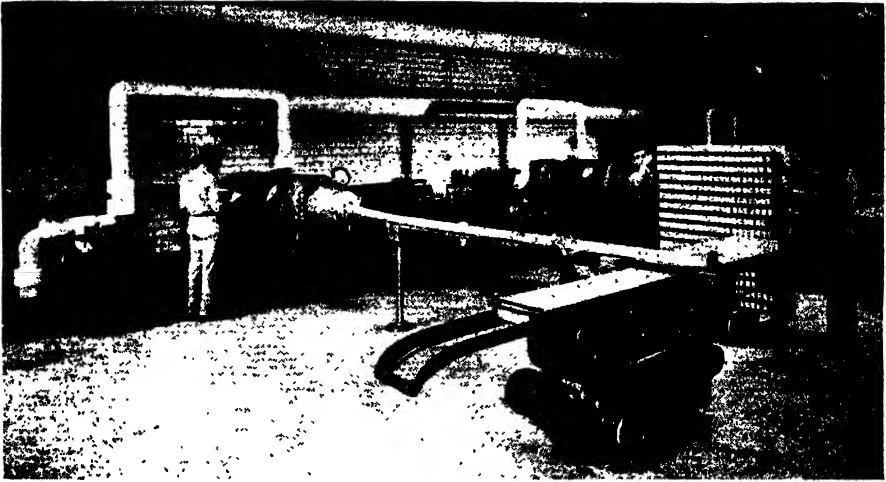


FIGURE 24.3. Soap Making. Soap is extruded, cut into strips three cakes long, then taken to a drying room before it is finally cut into bar size, stamped and wrapped. Courtesy The Procter & Gamble Company.

incorporated in them. The oil emulsion which forms when they are used has some dissolving action upon oils and greases. *Scouring soaps* contain solid material such as finely divided pumice or silica.

Transparent soap is made in more than one way. It may be produced by the "cold" process, in which oil and caustic are not boiled together but are mixed in just the right amount, warmed, and allowed to react over a period of days. The glycerine which is separated from soap in its ordinary method of preparation is left in the mixture when the cold process is employed. Sugar and alcohol may also be added in the preparation of soap by this method. In another method, ordinary soap is dissolved in alcohol, then recovered in transparent form by evaporation of the latter.

Soap cleans best in a slightly alkaline solution. Additives are sometimes included, particularly in the case of soap powders, to provide this alkalinity. They are known as *soap "builders."* They are substances such as sodium silicate, carbonate, phosphate, or borate, all of which hydrolyze to produce an alkaline solution. These compounds also help to soften the water, as described later.

The soaps of nearly all metals except sodium and potassium are insoluble in water and hence do not make effective detergents. Some of these are important in other ways because of their solubility in organic liquids, however. These include soaps of calcium, aluminum, lead, zinc, magnesium, barium, and lithium. All are used in lubricants.



FIGURE 24.4. Granulated Soap Manufacture. A pair of soap granules towers. Hot, liquid soap is sprayed through nozzles into the tops of the eight-story towers and falls as a fine mist. Heated air rises to meet the mist of soap, causing each drop to dry and puff up so that dried soap granules arrive at the bottoms of the towers. Courtesy The Procter & Gamble Company.

How Soap Cleans. In hot, very dilute solutions, sodium soaps appear to behave like other soluble sodium salts, i.e., they are dissociated into simple ions, as for example sodium and stearate ions from sodium stearate. But as concentration is increased and temperature is lowered, soap molecules and ions begin to associate in different ways to form larger ions and molecules. These are often negatively charged aggregates containing excess soap anions. It may well be that formation of these aggregates has something to do with the detergent action of soap. When soap

molecules or ions are mentioned in the explanation below it should be kept in mind that these may be aggregates, as well as simple units.

The cleaning action of soap is not thoroughly understood, partly because there are so many different kinds of "dirt" which can be removed from a surface with soap. The action of soap upon many oils is perhaps easiest to explain. These substances have a greater affinity for soap than they do for the surface being

cleaned. Soap molecules therefore work between the two, as shown in Figure 24.5.

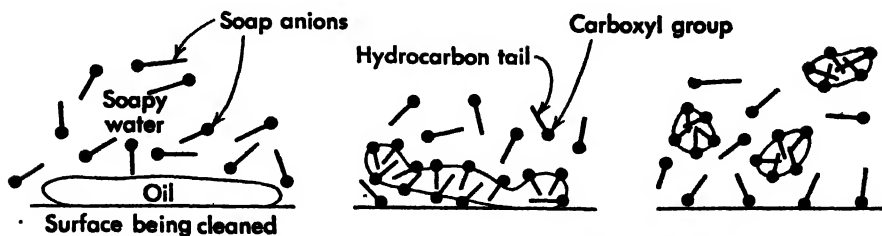


FIGURE 24.5. Cleaning With Soap. These drawings show how soap is believed to aid in cleaning oil from a surface. The action progresses from left to right.

This process is aided (a) by the molecular movements always present in liquids, and (b) by the mechanical action which usually accompanies the use of soap, such as movement of a brush, wash cloth, washing machine, etc. The soap anions which go to the oil surface are oriented, as shown in the drawing, with the hydrocarbon tails in the oil and the carboxyl group in the water. The oil is thought to be broken up by this combination of adsorption and movement. The tiny droplets produced will be negatively charged, because of adsorption of soap anions. This makes for a more stable suspension, since similarly charged droplets repel each other and therefore stay apart rather than coalescing to large drops. Suspensions of small drops of one liquid in another immiscible liquid are known as *emulsions*.

The effect of soap upon an oily or greasy dirt particle may well be the same as that just described, but soap also brings about the suspension of particles such as iron oxide or silica which are not oily. It is thought that these substances may adsorb soap anions the other way around, with the carboxyl group next to the particle and the hydrocarbon chain sticking out. This would give an oil-like nature to the surface of the particle, and might cause attraction of a second layer of soap ions or molecules, as shown in Figure 24.6.

Such multiple films of soap molecules have been prepared upon glass, and are therefore known to be possible, at least in

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the case of certain soaps.¹ These have been shown to be head to head and tail to tail as in the drawing. Such films are wet by

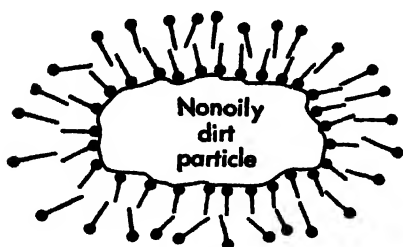
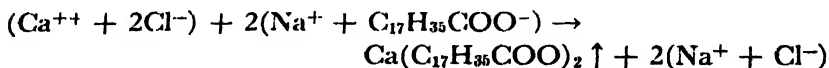


FIGURE 24.6. Mechanism of Detergent Action. Manner in which nonoily dirt particles may adsorb soap molecules or ions.

either oil or water, depending upon which end of the molecule happens to be outward in the last layer to be adsorbed. As many as 200 layers of soap molecules have been deposited on glass by use of special techniques.

Soap and Hard Water. Natural water contains as common ionic impurities chloride, sulfate, and bicarbonate anions, and cations of sodium, calcium, magnesium, and sometimes ferrous iron. When any of the last three of these are present in significant amounts the water is called *hard*. Hard water is objectionable because it forms a precipitate, or more properly a scum, with soap, causing that substance to lose its cleansing power until enough of it has been added to react with the hard water cations. The reactions are double decompositions, as for example that between calcium chloride and sodium stearate.



The insoluble calcium stearate rises to the top of the water as a scum, and this type of product largely accounts for the "ring around the bathtub" which forms when soap is used with hard water. Aside from soap difficulties, hard water also causes industrial problems, because when it is used in boilers it may cause corrosion, and precipitates may form (boiler scale) which reduce efficiency and lead to danger of a boiler explosion.

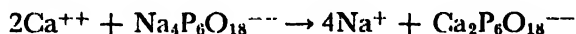
Treatment of hard water to overcome these objections is therefore of major importance in the home and in industry, and various methods of removing the offending calcium and magnesium

¹ Calcium, barium, and lead soaps have been used in multiple film experiments.

ions (*softening* the water) are in use. Thus, a sodium salt may be added which forms a precipitate with the undesirable ions, as washing soda, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

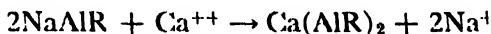


Sodium phosphate, tetraborate, and silicate behave similarly. Another method employs a substance which converts the undesirable ions into complex, *soluble* ions, unaffected by soap. Thus, Calgon² is a complicated phosphate which ties up calcium ions in this way.



Use of this product avoids scum formation before or after addition of soap and, in fact, calcium and magnesium soaps are dissolved if they have formed.

A third method involves passing the water through a porous solid in a replacement process where some other ion, usually sodium, is substituted for calcium and magnesium ions. Thus, the solid may be a complex sodium aluminum silicate. Using R for the anion:



These inorganic ion exchange materials go under various names, as zeolites, Permutit, Refinite, etc. There are also modern organic resinous materials used for this purpose which in a two-stage process can take out virtually all ionic impurities, leaving a product which is essentially as pure as distilled water.

The processes just described (except the last) do not purify hard water. They merely substitute for calcium and magnesium ions a cation (Na^+) which does not form scum with ordinary soap.

OTHER DETERGENTS

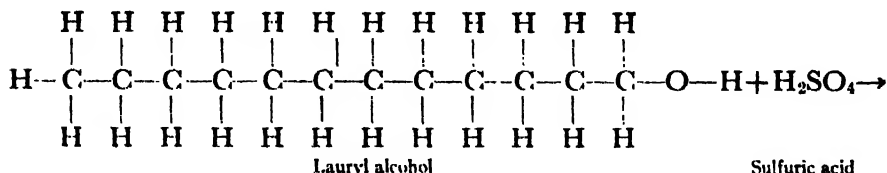
Soaps suffer from the disadvantage that they react with the inorganic calcium and magnesium salts present in many natural

² Sodium hexametaphosphate, $\text{Na}_6\text{P}_6\text{O}_{18}$, which dissociates into Na^+ cations and $\text{Na}_4\text{P}_6\text{O}_{18}^{--}$ anions.

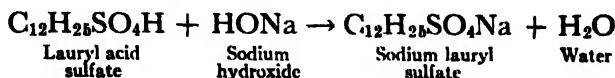
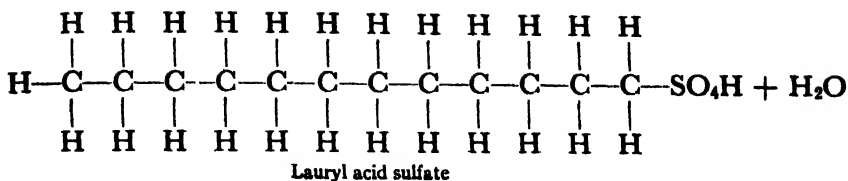
waters to form precipitates. This uses up soap and at the same time adds more "dirt" to the suspension in the form of the insoluble calcium or magnesium compounds. While this is overcome by using water softeners, it is also possible to employ other detergents besides soap which do not form precipitates with calcium or magnesium ions.

General Type of Molecule Required. An effective detergent appears to require a molecule which is oil soluble at one end and water soluble at the other. The oil soluble part, furthermore, must be fairly large, and quite often consists of a hydrocarbon chain of at least ten carbon atoms. However, the oil soluble part does not necessarily need to be a carbon chain; i.e., it may be a combination of a chain and a ring. It may also contain other elements, as nitrogen, along with the carbon. The water soluble end, too, does not need to be the carboxyl group present in soap. It can be the sulfate radical, or the sulfonate radical (SO_3H), or even a water soluble organic group which does not ionize off, such as a polyalcohol or a polyether. It can even be a negative ion, such as chloride, in "invert" soaps in which the hydrocarbon chain is part of a positive ion.

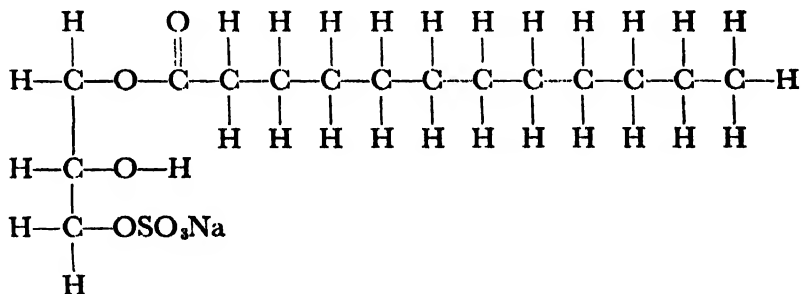
Sodium Lauryl Sulfate. One way to avoid precipitates with calcium and magnesium ions is to employ detergents, the calcium and magnesium salts of which are water soluble. Sodium lauryl sulfate (Dreft, Drene) is of this type. Lauryl alcohol³ is prepared by hydrogenation of fats from cocoanut and other oils. This is changed to an acid sulfate which is converted in turn to a sodium salt.



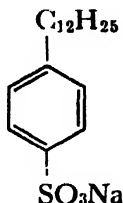
³ The lauryl alcohol of the organic chemist, $\text{C}_{12}\text{H}_{26}\text{OH}$, is used in the equations which follow. In the synthetic detergent field, however, "lauryl alcohol" is a term used to include a mixture of alcohols containing from 8 to 18 carbon atoms per molecule. Only about 40 per cent of this mixture is actually lauryl alcohol.



A number of other detergents, different from soap, are becoming available to the general public. Tide is a mixture of sodium "lauryl" sulfate and complex sodium phosphates.⁴ Vel and Halo are glyceryl esters in which one glyceryl valence is satisfied with a cocoanut fatty acid radical⁵ and another one with the SO_4Na radical, e.g.:



Swerl, Surf, Fab, and Trend are benzene derivatives containing a carbon chain and a sodium sulfonate group para to each other, e.g.:



The reader should note, however, that manufacturers sometimes change the composition of their products while continuing to sell them under the same name.

⁴ See Calgon, page 511.

⁵ Chiefly lauric acid, $\text{C}_{11}\text{H}_{23}\text{COOH}$.

Self Study Questions

1. Give four ways in which a surface may be cleaned and an example of each.
2. Explain how soap is thought to aid in cleaning.
3. Describe the preparation of sodium stearate from an appropriate fat. Include an equation. What other reaction product is made?
4. What volume of sodium hydroxide solution of density 1.13 g./ml. containing 12.0 per cent NaOH by weight would be theoretically required to saponify one kilogram of pure glyceryl laurate, $(C_{11}H_{23}CO_2)_3C_3H_5$?
Answer: 1.38 liters.
5. What is meant by soft soap? Marine soap? Scouring soap? Soap builders? Transparent soap? What chemical differences are present in each case, if any?
6. Why is soap wasted in hard water? What types of water softeners are available? Give examples.
7. What general characteristics must an effective detergent molecule possess?
8. What types of molecules are prepared in the newer detergents to yield products which will not form precipitates with calcium or magnesium ions?
9. Would you expect butyl stearate, $C_{17}H_{35}COOC_4H_9$ to be a satisfactory detergent? Would you expect sodium propionate, C_2H_5COONa to be a satisfactory detergent? Explain your answers.

Other Products of Chemistry

PERFUMES

Natural Perfumes. A perfume is a substance which is prepared for use because it pleases the sense of smell. Perfumes have been employed from earliest times, and the Bible and other books



FIGURE 25.1 Lavender Distillation. Steam distillation in the field as practiced in the lavender regions of Southern France. Courtesy Fritzsche Brothers, Inc.

of ancient origin refer to the use of such things as incense and fragrant oils or waters. The perfumes of the past were of natural origin, from plant parts such as flowers, bark, leaves, roots, wood, or seeds. These plant parts were treated to get the perfume by *distillation* with steam, as in the obtaining of lavender or

peppermint from the plants of that name; by *expression* of fragrant oils, as the pressing out of oil from orange or lemon peel; by *extraction* of perfume with fats, oils, or volatile solvents, as employed in obtaining essences from many flowers; by *enfleurage*, in which flower perfumes are absorbed by fats, oils, or volatile solvents after first being given off to the air or to some other gas, such as carbon dioxide.

Perfume Characteristics. It appears that perfume molecules must have certain characteristic properties besides a pleasing odor, or rather, to account for their odor. They must be sufficiently volatile to reach the organs of smell in the nose. They must apparently be somewhat water soluble and also somewhat oil soluble to penetrate the cells and reach the olfactory nerves. The lack of odor of many substances can be explained on this basis. Most solids, for example, are not sufficiently volatile to have an odor. Odorless methane and ethane gas are volatile and oil soluble but are not appreciably soluble in water. Ethylene and propylene, on the other hand, have a somewhat increased water solubility and also an odor. Grain alcohol is water soluble and volatile but is not sufficiently oil soluble to have a strong odor, whereas some of the higher molecular weight alcohols, with greater oil solubility, have a more powerful odor, in spite of their diminished volatility. On the other hand, alcohols of very high molecular weight lack odor because of low water solubility and low volatility.

The molecular structure of many of the substances responsible for characteristic plant odors has now been determined, and in addition a number of other substances have been prepared which have odors similar to those of plant products. Many chemicals are also now known which have pleasing odors unlike those from any known plants. A few substances with characteristic odors are given in Table 25.1.

Perfume Manufacture. Whereas the perfumes of a hundred years ago and earlier were of natural origin, present-day products tend more toward the artificial. Probably most perfumes on sale

TABLE 25.1 Compounds Responsible for Familiar Odors.

<i>The odor of</i>	<i>is largely due to, or simulated by</i>
ALMOND OIL	Benzaldehyde
CLOVE OIL	Eugenol
LEMON OIL	Citral
VANILLA	Vanillin
VIOLET	Ionone
OIL OF WINTERGREEN	Methyl salicylate
BANANA	Amyl acetate
PEPPERMINT	Menthol
CLOVER	Amyl salicylate
CARNATION	Iso-eugenol
LILAC	Terpineol

now are blends of synthetic materials, fragrant substances of natural origin, solvents and substances added to retard evaporation and to give persistency to the odor. The synthetic odor producer may be one which simulates a natural fragrance, such as ionone (violets), or it may be a mixture of substances which gives a distinctive odor not found in nature. If a natural odor is being duplicated, the more expensive products will also probably contain some of the natural perfume along with synthetic substitutes. The persistency of odor after application of a perfume is important. This is produced by including a material of low volatility which not only tends to remain on the surface where the perfume is being used but also retains in solution or as an adsorbed film the chemicals responsible for the odor, so that these are given off slowly for some time. Examples of such additives are natural products such as balsams, gums, and musks, and synthetic materials like ethyl phthalate or coumarin. These substances may be essentially odorless, or they may have an odor of their own which contributes to the over-all scent.

COSMETICS

These are preparations used for improving the appearance of skin, hair, nails, and teeth. They have been employed for thousands of years, as shown by the finding of Egyptian ointment jars of about 3500 B.C. and of descriptions of beautifying (?)

techniques used by early Egyptian women which included painting the region under the eyes green and that over the eyes black, and the dyeing of nails, palms of the hands, and soles of the feet with henna. The Romans, too, whitened their skin with chalk and white lead (!), and used eye darkener, rouge, and depilatories. Cosmetics were widely employed in Europe and Great Britain during medieval and later periods, but not without criticism, as attested by part of a bill introduced into the English parliament in 1770.

That all women of whatever age, rank, profession or degree, whether virgins, maids or widows, that shall, from and after such Act, impose upon, seduce, and betray into matrimony, any of His Majesty's subjects, by the scents, paints, cosmetic washes, artificial teeth, false hair, Spanish wool, iron stays, hoops, high-heeled shoes, bolstered hips, shall incur the penalty of the law in force against witchcraft and like misdemeanors and that the marriage, upon conviction, shall stand null and void.¹

Cold Cream. These products are most simply emulsions of water droplets in oil, with a stabilizing agent of soap made by the action of borax upon beeswax. Mineral oil, beeswax, water, and borax were the original ingredients, but modern cold creams may contain other oils and waxes, antioxidants, vitamins, hormones, perfumes, etc. Some of these additives, such as vitamins and hormones, change the nature of the cream from a simple cosmetic to a drug.



FIGURE 25.2. Adding Perfume to Batch of Night Cream. Courtesy Bonne Bell, Inc.

¹ *Picassc, Art of Perfumery* (1879).

Vanishing Cream. Vanishing cream is basically water containing stearic acid, glycerine, and a soap. The insoluble stearic acid is present in finely divided form and the whole is stabilized by the soap and to some extent by the glycerine. Modern vanishing creams often sell under other names such as facial cream, powder base cream, and hand cream. Some also are medicated, making them drugs in a legal sense. Deodorant creams are vanishing creams in many cases. These are mixtures which either (a) sterilize perspiration, preventing its decomposition to products of unpleasant odor, or (b) inhibit the formation of perspiration by the presence of an astringent substance, commonly aluminum or zinc salts. These last deodorants, known as antiperspirants, are legally regarded as drugs, since they affect a body function.

Face Powder. Powders (face, talcum, body, baby, foot, etc.) are probably used more commonly than any other cosmetic. Chief of these is face powder, employed by at least 90 per cent of American women. This is a mixture of pigments which, to be effective, must have certain qualifications. It must first be of the correct *shade*, and must not vary significantly in shade from one container to another of the same product. Color is imparted by using earth pigments, such as ochre or the siennas (page 492), or one or more of several dozen certified lakes (page 251). *Covering power* is the next most important property. Zinc oxide and/or titanium oxide are usually added to give increased covering power. *Slip* is the ability of powder particles to slide over one another readily, so that the product can be applied without too much drag, or lump formation. This necessary property is supplied by talc, and the latter is commonly the most plentiful ingredient in face powders. *Adhesion*, which makes the powder stay on the skin, is increased by including zinc stearate and other soaps. *Odor* is supplied by addition of perfume. Other properties of face powders are also controlled by manufacturers, but these five are probably the chief ones to consider if the powder is to have a successful sale.

Lotions. These are fluid mixtures to be rubbed on the skin for various purposes. *Hand lotions* are often simply mixtures of glycerine and rose water. Emulsion lotions, chiefly water, and often



FIGURE 25.3. Skin Cleansing Lotion. A vacuum filling machine is being used. Courtesy Bonne Bell, Inc.

containing triethanolamine soaps, are also used for this purpose. Alcohol is usually one of the components of *shaving lotions*, and is frequently present in high concentration. These lotions may also contain astringents, such as alum or zinc sulfocarbolate,² and menthol is often added to give a feeling of coolness to the skin.

Other Cosmetics. Dentifrices are products which aid the toothbrush in cleaning the teeth. *Tooth powders* are chiefly polishing agents, often precipitated chalk or calcium phosphates.

² Hydrated zinc phenyl sulfate, $\text{Zn}(\text{C}_6\text{H}_5\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$.

Tooth pastes contain in addition a binder, frequently a starch-water-glycerine mixture which makes the product plastic in nature; a small amount of oil is also included to lubricate the product so that it can be squeezed from the tube. Foaming

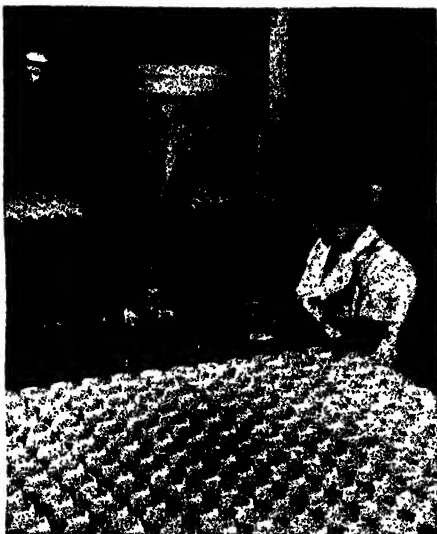


FIGURE 25.4. Cream Shampoo. This oil-in-water emulsion is put into jars cold by means of the piston jar-filler shown. Courtesy Bonne Bell, Inc.

agents, flavorers, and sweeteners are usually included in both pastes and powders. *Depilatories*, for removing hair, commonly contain soluble metal sulfides or acid sulfides, including those of sodium, calcium, strontium, or barium. These salts cause hair to swell and become easily scraped off, probably because they are attracted to the disulfide linkages (—S—S—) known to be present in the keratin molecules of hair. Some recent depilatories which lack the odor of hydrogen sulfide found in metallic sulfide preparations are compounds of thioglycollic

acid, HSCH_2COOH . Calcium or glyceryl thioglycollates are used in mixtures such as pastes or liquids.

Nail lacquers are usually solutions of cellulose nitrate in suitable solvents, including banana oil (amyl acetate). Like the lacquers described earlier (page 499), these also contain plasticizers, resins, and coloring agents. *Lacquer removers* frequently contain acetone and ethyl acetate. *Suntan preparations* have in them a substance which absorbs ultraviolet light for several hours after application and hence prevents sunburn. A number of such substances are known, including menthyl salicylate, benzyl salicylate, glyceryl salicylate, fenchyl anthranilate, menthyl anthranilate, butyl benzal acetone oxalate, sesame oil, and others. *Permanent wave preparations* are alkaline solutions which aid in the stretch-

ing of hair. When the stretching is caused to take place around rods, the outer side of each curled hair is made somewhat longer than the inside; since this change is a relatively permanent one the hair continues to retain its curl.

DYES

Color. White light consists of a mixture of radiations of various wave lengths which by themselves create different effects upon the retina of the eye, known as colors. In the order of increasing wave length these appear as violet, indigo, blue, green, yellow, orange, and red, the entire visible band covering from about 4000 angstroms (page 13) to about 7000 angstroms in wave length. This is of course only a small portion of the entire span of known radiations, even when the invisible ultraviolet and infrared light regions on either side are included. When an object transmits all of these colored portions of white light equally and to a high degree it is called transparent, and the higher the percentage transmittance the greater the transparency. When it absorbs them all it is opaque and black in color. An object which absorbs colored light unequally, i.e., one color to a greater degree than another, is said to be colored. The part of the light not absorbed, which is reflected or transmitted, then determines the color. If a surface absorbs all light but green, the reflected green light causes us to regard the object as being green in color. It will also appear green if the reflected light is a mixture of blue and yellow, so that one cannot always make a correct conclusion as to the characteristics of reflected or transmitted light by a simple visual examination.

The unequal light absorption which produces color is characteristic of many familiar natural and synthetic materials. The group of organic substances, known as dyes, and used for coloring cloth, is the important class now under consideration.

Chromophores. Most organic substances absorb light in the ultraviolet region, but not in the visible, so that they are without visible color. But when certain groups of atoms are present in

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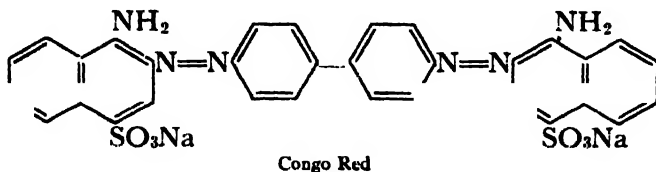
the molecular structure absorption of colored light in the visible region takes place and color therefore becomes apparent. These groups of atoms which by their presence create color are known as *chromophores* from the Greek *chroma*, color, and *phoros*, bearer. There are many such groups. Two common ones are the *azo* group and the *quinoid* group, both shown below.



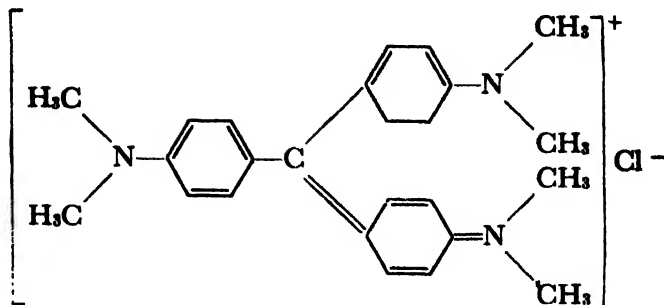
Fundamentally, these structures create color because they contain electrons which tend to resonate (vibrate) with the frequencies of visible light, and under these conditions they appear to be capable of absorbing the light. Practically nothing is known about the specific mechanism of light absorption by electrons, but the reader can perhaps better understand what scientists believe is the general process by the facetious analogy of the child who avoids medicine by violently shaking his head and yelling. He can still be made to absorb the medicine if the spoon can be made to vibrate in phase with, and at the same frequency as, his head. And after absorbing the medicine he would shake his head still more violently, if he behaved like an electron which has absorbed radiation.

The unique feature about such colored substances is not that they absorb radiation, since all organic compounds do so, but that the absorption is in the visible region, whereas most substances absorb in the shorter wave length ultraviolet. These chromophore groups therefore possess electrons which vibrate more slowly than usual, permitting them to absorb the lower frequency, visible light.

An example of a dye containing the azo group is Congo Red.



An example of a dye containing the quinoid structure is Crystal Violet.



Other Groups in Dyes. Besides the color-imparting group, other groups have been found to intensify colors, or to cause a shift in color to a new, desirable shade. These are the *auxochromes* (color increasers). They include the —NH_2 , —NHR , —NR_2 , —OH , —OCH_3 , —I , —Br , and —Cl groups. Still other groups are added to improve water solubility during the manufacture or application of some dyes. Chief of these is the $\text{—SO}_3\text{H}$ or sulfonic acid group.

Methods of Dyeing. The simplest method of dyeing is to immerse the article being colored into a solution of the dye. Known as direct, or substantive dyeing, this process is employed most often with wool or silk. These fibers are amphoteric proteins, capable of attracting and holding dye ions. If D^+ is used to represent a positive dye ion such as that of Crystal Violet above, and if P^- is the negative part of a protein molecule, then the dyeing of wool or silk can be illustrated by the chemical change:



Whereas the fiber P was essentially colorless, the combination of dye and fiber DP is now a stable, colored product.

Cellulosic material on the other hand, such as cotton, linen, or cellulose rayon, lacks these ionic properties, and it is more difficult to dye directly. *Mordant* dyeing is often used with this type of fiber. This involves first the precipitation of a metallic hydroxide in the cloth followed by application of the dye. The

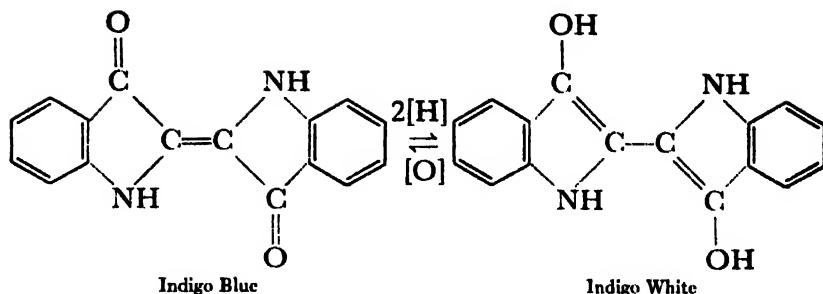


FIGURE 25.5. Dyeing. Unloading dyed fabric from dyebox. Courtesy S. Blickman, Inc.

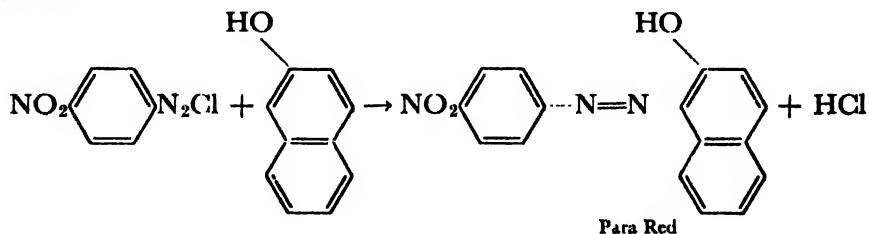
precipitated hydroxide has an affinity for both the cloth and the dye, hence it can be thought of as holding them together by “biting” into each. This accounts for the term mordant, from the Latin *mordere*, to bite. The combination of the hydroxide and the dye, called a *lake*, may be of different shades depending upon which hydroxide is used, e.g., whether that of aluminum, iron, chromium, tin, or something else.

In a third type of dyeing procedure a chemically altered form of the dye, or perhaps a smaller molecule which will be but part of the final dye molecule, is first put on the cloth. A chemical reaction is then made to take place in which the dye is formed on the cloth. If the dye is first applied in reduced, soluble form, and is then oxidized by the air to the final, insoluble colored product, the process is known as *vat* dyeing. The commonest dye to be so applied is probably *indigo*. Its reduced and oxidized forms are shown on the opposite page.

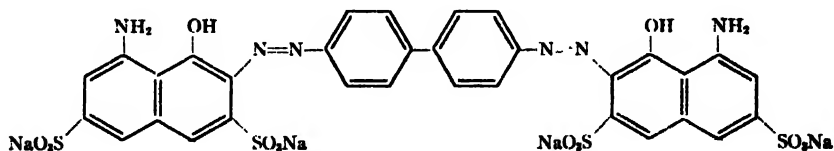
Other oxidizing agents, such as chlorates or dichromates, are also used in the formation of this type of dye. Azo dyes are likewise frequently formed in place from smaller molecules in a



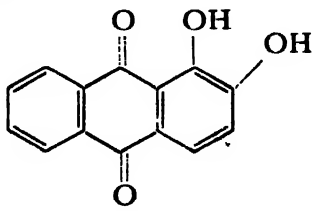
process known as *ingrain dyeing*. Formation of Para Red is an example. Beta naphthol is first put on cloth and then allowed to react with diazotized *p*-nitro-aniline, as shown in the reaction below.



Diamine Blue is an example of a substantive dye.



Alizarin is a familiar mordant dye. Note the presence of the quinoid chromophore.



Molecular weight measurements indicate that some dyes, and probably all of them, are associated in solution, so that their molecules are much larger than the formula would indicate.

Thus, Congo Red (page 524) has been found to have a molecular weight of approximately 8000, indicating that it occurs as aggregates of about twelve of the molecules shown on page 524, on the average.

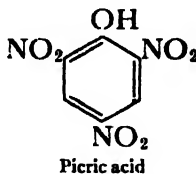
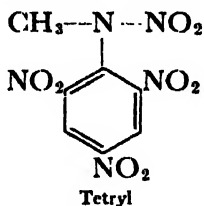
EXPLOSIVES

An explosive is a substance which can be made to decompose suddenly, with evolution of light and heat, into products which tend to occupy a very much larger volume than that originally required. If the explosion takes place in a confined space, the high pressure developed by the products as they seek to expand accounts for the familiar effects produced.

Types. Explosives vary in the ease with which they decompose, from the sensitive detonators, such as mercury fulminate,



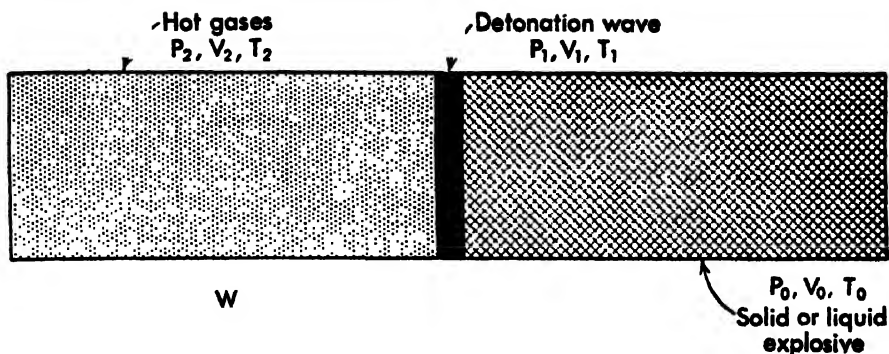
through boosters such as tetryl or picric acid



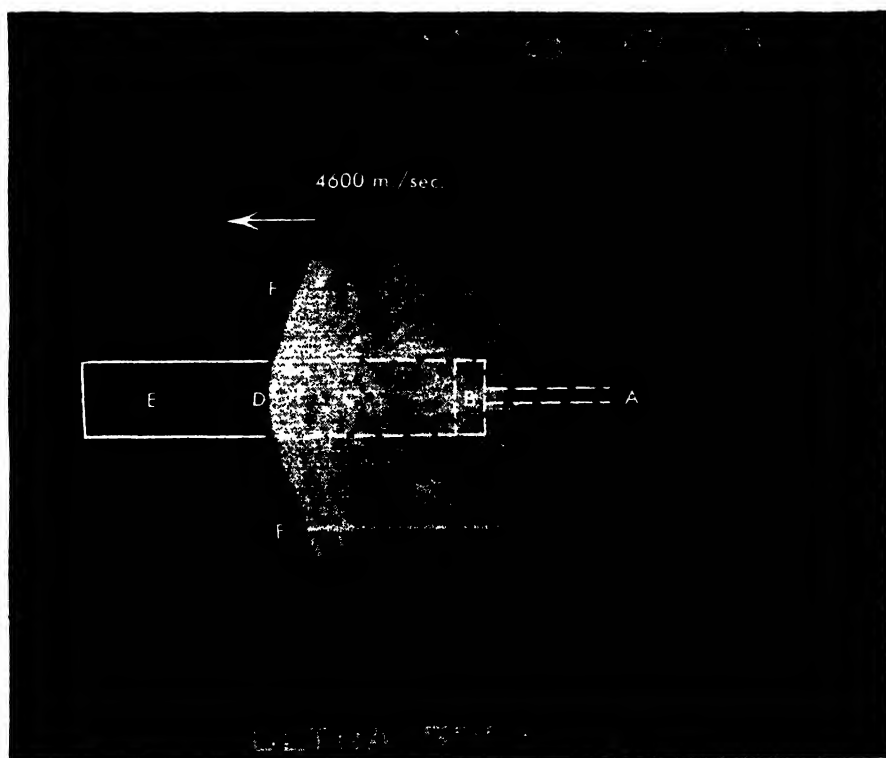
to the more difficultly exploded products such as TNT.



Detonators are exploded by percussion, fire, or electricity. The percussion method would be represented by the hammer of a gun, blasting fuse is an example of the use of fire and electric blasting caps are detonated by applying current to a high resistance bridge wire. The explosion of the detonator then causes the other substances present to explode. TNT is difficult to



(a)



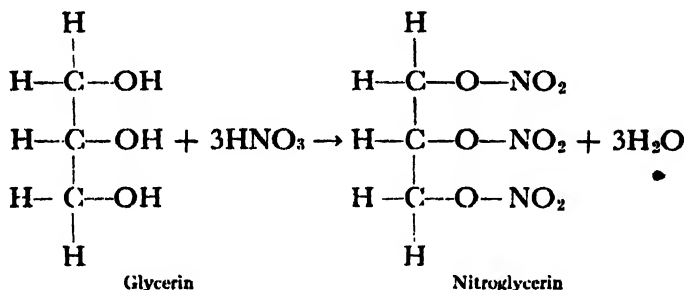
(b)

FIGURE 25.6. Detonation of a Column of Explosive. (a) Schematic diagram. The detonation wave (black band), at a temperature which may reach 4000°C . and having a pressure of 100,000 atmospheres or more, travels from left to right at from 1500 to 8500 meters per second. (b) Instantaneous photograph of exploding TNT. The detonation wave here is travelling at 4600 meters per second. Courtesy Hercules Powder Company.

detonate even under these conditions, hence a booster is commonly included when this product is used.

Explosives also vary in the rate at which they explode. Those having a higher rate of detonation, such as TNT or plutonium, are used in bombs and shells, while those with lower rates of detonation, such as nitrocellulose, are employed in guns and rifles as propellants.

Dynamite. The term “dynamite” is used for a great many explosives, some of which contain nitroglycerin or nitroglycol, others nitrostarch and still others ammonium nitrate. Nitroglycerin is made by treating glycerine with nitric acid in the presence of a dehydrating agent. Wood pulp is employed as a



diluent in most dynamites using a liquid explosive such as nitroglycerin. *Gelatin dynamites* contain, among other things, a varying amount of nitrocotton. They may also contain ammonium nitrate. *Blasting gelatin* is a very powerful explosive consisting of only nitrocotton and nitroglycerin.

Self Study Questions

1. What four general methods are employed in obtaining natural perfume? What plant parts are used as sources of perfumes?
2. What general properties must a liquid or solid possess to account for its affecting the olfactory nerves? Explain on the basis of the theory given why water and polyethylene are odorless.
3. Name several substances responsible for, or which simulate, the odor of natural products.

4. What types of products are used in most present-day perfumes?
5. Give evidence as to the early use of cosmetics.
6. What is the most basic composition of cold cream? How is it stabilized?
7. What is the chemical nature of vanishing cream?
8. What five properties must a successful face powder possess? What substances are used to improve each of these?
9. Tell something of the chemical composition of lotions, dentifrices, depilatories, nail lacquers, lacquer removers, suntan preparations, and permanent hair waving preparations.
10. Account for the color of a dye in fundamental terms. What is a chromophore group? An auxochrome group? Give examples of each.
11. What general methods of dyeing are in use? What is a mordant? A lake? Give examples.
12. Give examples of three types of explosives based upon the ease with which they are detonated.
13. What are two types of explosives, based upon the speed with which they explode? Give examples of each.
14. Classify (*a*) gunpowder, (*b*) a gasoline vapor—air mixture, (*c*) ${}_{92}\text{U}^{235}$, as to whether they are detonators, boosters, explosives, or propellants.

PART NINE

Supplementary Problems

XXVI

Supplementary Problems

Graphs, Exponents, Units of Measurement. The reader may wish to reread the mathematical review starting on page 9 before beginning to work on these problems. Answers are given on page 553.

1. Construct a graph showing the change of density of water between zero and $10^{\circ}\text{C}.$, using the data on page 114. Note that it is customary to make the X axis or abscissa the independent variable (temperature) and the Y axis or ordinate the dependent variable (density).

2. From the graph on page 174 showing saturation solubilities of salts in water, what weight of potassium nitrate can be dissolved by 100 g. of water at $30^{\circ}\text{C}.$?

3. In the same graph, what weight of potassium alum will precipitate from a saturated solution containing 100 g. of water as it cools from $90^{\circ}\text{C}.$ to $10^{\circ}\text{C}.$?

4. What weight of sodium chloride can be dissolved by a liter of water at $50^{\circ}\text{C}.$ (graph, page 12; density data, page 114)?

5. Write Avogadro's Number, 6.023×10^{23} , without using exponents.

6. Rewrite the quantity 0.00013 g. as 1.3×10^{-n} , where n is the proper exponent.

7. A cubic meter or stere is 100 cm. on a side. How many cubic centimeters are in a stere? Express this by using 10 with an exponent. How many liters are in a cubic meter?

8. 6.023×10^{23} molecules of grain alcohol weigh 46 grams. Calculate the weight in grams of one grain alcohol molecule.

536 Supplementary Problems

9. Convert 500°K . to the corresponding Centigrade and Fahrenheit temperatures. Convert 500°F . to the corresponding Centigrade and Kelvin temperatures.

Percentage Composition

EXAMPLE: What is the percentage of carbon in table sugar (sucrose), $\text{C}_{12}\text{H}_{22}\text{O}_{11}$?

The molecular weight of table sugar is found by adding up the various atomic weights given in the atomic weight table, i.e., carbon, 12×12.01 , hydrogen, 22×1.008 , oxygen, 11×16.00 . The molecular weight found in this way is 342.30. The fractional amount of carbon in table sugar is therefore $\frac{144.12}{342.30}$ and the percentage of carbon is $\frac{(144.12)(100)}{(342.30)}$ or 42.10 per cent.

10. Calculate the percentage of each element in the following substances: sodium chloride (NaCl , common salt), sodium bicarbonate (NaHCO_3 , baking soda), sodium palmitate ($\text{NaO}_2\text{C}_{16}\text{H}_{31}$, one of the chief components of soap).

11. Calculate the approximate percentage composition of water (a) made from the heaviest isotopes listed in the atomic weight table, and (b) made from the lightest isotopes listed.

12. What percentage of water is present in the hydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$? What percentage of oxygen is present in the hydrate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$?

Problems Based upon Boyle's and Charles' Laws. Following are problems which require use of Boyle's Law ($V_s/V_f = P_f/P_s$) and Charles' Law ($V_s/V_f = T_s/T_f$). It often becomes necessary also in gas chemistry to calculate the change in volume of a gas which would occur if both pressure and temperature were changed. This can be done by applying the two laws sequentially, i.e., an intermediate volume is calculated from the starting gas volume by using the Boyle's Law equation at constant temperature (the initial temperature). The final volume is then calculated from the intermediate volume at constant pressure (the final pressure) by using Charles' Law.

For example, if a sample of gas has a volume of 500 ml. at 23°C. and 735 mm. pressure, one would calculate the volume at *standard conditions* (0°C. and 760 mm. pressure) in the following manner. First Boyle's Law could be applied, assuming the pressure to change from 735 mm. to 760 mm. at 23°C.

$$\frac{500}{V_i} = \frac{760}{735}$$

V_i , the intermediate volume, comes out to be 484 ml. The final volume can then be calculated from this by applying Charles' Law, assuming a constant pressure of 760 mm.

$$\frac{484}{V_f} = \frac{296}{273}$$

In practice such problems are solved without the finding of the intermediate volume, i.e.,

$$(500) \left(\frac{735}{760} \right) \left(\frac{273}{296} \right) = 446 \text{ ml.}$$

The final volume at standard conditions is 446 ml.

The two laws can be combined into one equation. Using the symbol V_i for the intermediate volume, Boyle's Law gives:

$$(1) \quad V_s/V_i = P_f/P_s$$

and

$$(2) \quad V_i = (V_s)(P_s)/(P_f)$$

For the Charles' Law calculation:

$$(3) \quad V_i/V_f = T_s/T_f$$

Now if the expression for V_i in (2) be used in (3), V_i drops out.

$$(4) \quad \frac{(V_s)(P_s)}{(V_f)(P_f)} = \frac{(T_s)}{(T_f)}$$

If starting pressure, temperature and volume are put on one side and the corresponding final values on the other, a symmetrical expression is obtained.

$$\frac{(P_s)(V_s)}{(T_s)} = \frac{(P_f)(V_f)}{(T_f)}$$

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This is the combined equation which results when Charles' Law and Boyle's Law are used in one calculation. Solving the previous problem with this equation, we now obtain:

$$\frac{(735)(500)}{(296)} = \frac{(760)(V_f)}{(273)}$$

and V_f again comes out to be 446 ml. However, it is better mental training to think out the solutions to problems of this type by the first method, rather than to use a general equation in a superficial manner (see page 547).

13. A specimen of gas has a volume of 38.4 ml. at 20°C. What will the volume become if the gas cools, at constant pressure, to 10°C.?

14. A sample of helium at 0°C. and 760 mm. pressure (standard conditions) has a volume of 500 ml. If there is no temperature change, what volume will the gas occupy if the pressure is increased to 800 mm.?

15. Dry nitrogen gas has a volume of 136 ml. at 30°C. and 741 mm. pressure. What will the volume become at standard conditions?

16. A gas specimen has a volume of 45.7 ml. at 25°C. and 750 mm. pressure. The pressure changed to 758 mm., and the volume of the gas became 46.3 ml. Did the temperature also change? To what?

Dalton's Law Calculations. A further complication results in Boyle's and Charles' Law problems if the starting sample of gas is "wet," i.e., if it contains water vapor, and the final calculated volume must be that of a dry gas. The water vapor pressure of the wet gas must be known. If this gas has been collected "over water" (water being the retaining liquid), then the humidity can be assumed to be 100 per cent, and the water vapor pressure will be the saturation value for that temperature. This pressure must be subtracted from the total gas pressure, in a process like that used on page 51 to illustrate Dalton's Law of

partial pressures. Water vapor saturation pressures are given in Appendix B, page 561.

Consider the following problem: A gas is found to have a volume of 37.8 ml. when measured over water at 26°C. and 740 mm. pressure. What will its volume be when it is dry, at standard conditions?

This is set up as before, but the original pressure of the gas over water, 740 mm., is corrected by subtracting the water vapor pressure.

$$\frac{(740 - 25)(37.8)}{(299)} = \frac{(760)(V_f)}{(273)}$$

and the final volume is 32.5 ml.

17. A sample of air saturated with water vapor at 27°C. has a pressure of 748 mm. If a sample of this air were dried without change of volume or temperature, what would its pressure become (Appendix B)?

18. If the air in problem 17 had a relative humidity of 45 per cent, what would the final pressure become upon drying?

19. A specimen of gas saturated with water vapor has a volume of 57.6 ml. at 18°C. and 745 mm. pressure. Calculate what the volume of the gas should become when it is dry and at standard conditions.

Graham's Law Calculations. Another gas calculation is that of the relative rates of diffusion of two gases. For example, if two automobile tires are filled with different gases at the same pressure and temperature, and these tires develop identical punctures, it is possible to calculate which gas would escape the faster, and how much so. The rates of diffusion are proportional to the average gas velocities and a ratio of the latter can be found from kinetic energies. These are the same for the two gases at the same temperature. Using hydrogen and oxygen as our two gases, for example, we obtain the following:

$$1/2mv^2 \text{ for hydrogen} = 1/2mv^2 \text{ for oxygen}$$

and

$$(mv^2)_H = (mv^2)_O$$

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Substituting the *molecular* masses, 2 avograms for hydrogen and 32 avograms for oxygen:

$$(2v^2)_H = (32v^2)_O$$

and

$$\frac{(\text{velocity hydrogen})^2}{(\text{velocity oxygen})^2} = \frac{32}{2} = \frac{16}{1}$$

Taking the square root of each side,

$$\frac{\text{velocity hydrogen}}{\text{velocity oxygen}} = \frac{4}{1}$$

or hydrogen will diffuse four times as rapidly as oxygen. In general, under similar conditions, *the diffusion rates of two gases are inversely proportional to the square roots of their molecular weights.* This is a slightly modified form of one of the early laws of chemistry, *Graham's Law*.¹

20. A hydrogen molecule moves at the rate of about a mile a second, on the average, at room temperature. What will be the average velocity of a carbon dioxide molecule* at room temperature, if it has the same kinetic energy as a hydrogen molecule?

21. A methane molecule (CH_4) has a mass of 16 avograms, while that of heptane (C_7H_{16}) is 100 avograms. How much faster will methane diffuse than heptane vapor, conditions being the same?

Gas Law Deviations. It should finally be pointed out that while the gas laws are often used in the simple mathematical form given here, to calculate how gases should theoretically change in volume as temperature, pressure, or relative humidity is varied, gases themselves do not behave exactly in this manner, and for this reason there are slight deviations between predicted and observed results. For example, 100 liters of air at 0°C . and one atmosphere pressure should become one liter at 0°C . and 100 atmospheres pressure. (Why?) Actually the volume at the

¹ The diffusion rates of two gases are inversely proportional to the square roots of their densities. (Graham's Law).

higher pressure is 0.973 liter. The reasons for these small errors in the gas laws are fairly well understood, and in careful calculations corrected gas laws can be used which lead to a more accurate result. A theoretical gas which behaves exactly as predicted by the gas laws as stated here is called a *perfect* gas. Hydrogen and helium come the closest to being perfect gases.

Relative Humidity

22. What is the water vapor pressure at 25°C., when the relative humidity is 35 per cent (Appendix B)?

23. The water vapor pressure in a room is 15.3 mm. at 25°C. What is the relative humidity?

24. The water vapor pressure in a hall is 0.025 atmosphere at 23°C. Should the air be moistened or dried to insure a more comfortable audience?

25. Air coming into a room has a relative humidity of 93 per cent at 90°F. What must the temperature of a water spray be if, when the air is later warmed to 75°F., it will have a relative humidity of 60 per cent?

Molecular Weight from Gas Density and Vice Versa. By gas density is generally meant the weight of a liter of gas at standard conditions. Since the gram molecular weight of a gas is the grams of gas present in 22.4 liters at standard conditions, gas density $\times 22.4$ will give the molecular weight, and conversely (molecular weight)/22.4 will be the gas density.

EXAMPLES: Radon has a gas density of 9.91. What is its molecular weight?

$$9.91 \times 22.4 = 222$$

The molecular weight of carbon monoxide is 28.

What is the density of this gas?

$$\frac{28}{22.4} = 1.25$$

Calculation of molecular weight is also possible, but more complicated, when the weight of other than a liter of gas is specified at temperatures other than standard.

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EXAMPLE: A specimen of ethane gas has a volume of 372.4 ml. when collected over water at 26°C. and 748 mm. pressure, and weighs 0.433 g. What is the approximate molecular weight of ethane?

The volume which the gas would occupy dry, at standard conditions, is first calculated.

$$\frac{(372.4)(748 - 25)(273)}{(760)(299)} = 323 \text{ ml.}$$

The molecular weight is then found as before.

$$\frac{323}{22,400} = \frac{0.433}{X} \qquad X = 30$$

26. A liter of methane gas weighs 0.72 gram under standard conditions. Calculate the approximate molecular weight of methane.

27. Calculate the gas density of ethane, C_2H_6 , from its molecular weight.

28. A specimen of nitrogen gas collected over water has a volume of 428 ml. and a weight of 0.479 g. The temperature of the gas is 23°C. and the pressure is 756 mm. Calculate the approximate molecular weight of nitrogen from these data.

29. From the molecular weight of carbon monoxide as obtained from atomic weights, calculate the expected weight of a sample of this gas collected over water at 20°C. and 760 mm. pressure if the volume under these conditions is 47.8 ml.

30. Ammonia has the formula NH_3 . What is the molecular weight of this gas? What percentage of nitrogen does it contain? What will be its vapor density? What volume will 50 g. of this vapor occupy at 740 mm. pressure and 25°C.?

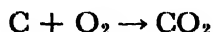
31. What volume will 20 grams of nitrogen occupy when measured over water (page 561) at 30°C. and 750 mm. pressure?

Calculations Based upon Chemical Change. When the chemist knows the formulas and molecular weights of substances taking part in chemical changes, and the manner in which they

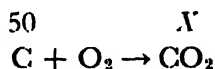
react, he can then calculate the necessary weights of materials to use in the process and the expected weight of product.

EXAMPLE: What weight of carbon dioxide will be formed when 50 grams of carbon is burned with an excess of oxygen?

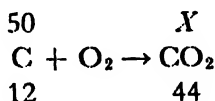
A convenient procedure in the solving of this, the commonest type of calculation in chemistry, is that described under the nut and bolt example on page 9. The balanced equation is first written.



The weights in the problem (X grams carbon dioxide, 50 grams carbon) are put over the proper formulas.



The standard weights for this chemical change (atomic and molecular weights) are put underneath.



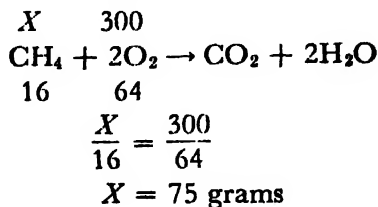
A mathematical equation is now made with these four quantities, keeping each in its same relative position. X is isolated and found.

$$\frac{50}{12} = \frac{X}{44}$$

$$X = \frac{(50)(44)}{(12)} = 183 \text{ grams}$$

Consider one more problem of this type.

What weight of methane gas will be needed to react with 300 grams of oxygen to form carbon dioxide and water?

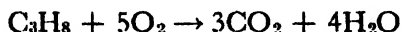


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Observe carefully that 64 grams of oxygen is used for the standard weight of this substance. This is *two* gram molecular weights, since there are this number indicated in the balanced equation. Failure to use the proper *number* of molecular weights is one of the common errors made by beginners. Common, too, are errors in the molecular weights caused by failure to take the proper number of atomic weights. Thus, beginners sometimes get a molecular weight of 13 for methane ($12 + 1$) instead of 16 ($12 + 4$).

Another common type of calculation involves gas volumes.

EXAMPLE: What volume of oxygen will react with 50 liters of propane to form carbon dioxide and water? Assume the propane to be at standard conditions when the volume measurement is made.



When a problem involves gas volumes, the gram molecular volume, 22.4 liters, should be brought to mind. It is apparent from the equation above that five gram molecular weights of oxygen react with one of propane. A gram molecular weight of a gas at standard conditions occupies 22.4 liters; hence 112 liters of oxygen are needed to burn 22.4 liters of propane. These quantities constitute the standard volumes used in the proportion.

$$\begin{array}{rcc} 50 & X \\ \text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O} \\ 22.4 & 112 \\ \frac{50}{22.4} = \frac{X}{112} & X = 250 \text{ liters of oxygen} \end{array}$$

A simplification is possible in this type of problem, since the numbers of gas molecules in the balanced equation are proportional to the volumes, from Avogadro's Law. Hence:

$$\frac{50}{1} = \frac{X}{5} \quad X = 250 \text{ liters of oxygen}$$

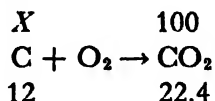
One can conclude by merely inspecting the balanced equation that the volume of oxygen required will be five times the volume

of propane if both gases are assumed to be pure and at the same temperature and pressure.

The third type of calculation is a combination of the other two.

EXAMPLE: What weight of carbon must be burned in order to form 100 liters of carbon dioxide at standard conditions?

The proportion will now be of the type $W_1/W_2 = V_1/V_2$, where the numerator values will be those given in the problem (X grams carbon, 100 liters carbon dioxide) and the denominator values will be the standard weight (12 grams carbon) and the standard volume (22.4 liters carbon dioxide).



and

$$X = 54 \text{ grams.}$$

Summary. The three types of calculations just described all involve direct proportions. The three general types are:

$$(1) \frac{W_1}{W_2} = \frac{W'_1}{W'_2} \quad (2) \frac{V_1}{V_2} = \frac{V'_1}{V'_2}$$

$$(3) \frac{W_1}{W_2} = \frac{V_1}{V_2} \quad \text{or} \quad \frac{V_1}{V_2} = \frac{W_1}{W_2}$$

W signifies a weight and V a gas volume.

The type of proportion depends upon the problem: (1) applies to problems dealing only with weights, (2) to those having to do only with gas volumes, and (3) to those in which both a weight and a gas volume are specified.

32. What weight of oxygen will be needed to convert 20 grams of phosphorus to phosphorus pentoxide?

33. How many grams of carbon dioxide will be formed when 50 grams of methane, CH_4 , is burned?

34. Iron reacts with oxygen at high temperatures to form magnetic iron oxide, Fe_3O_4 . What weight of this oxide will be formed by the burning of 10 grams of iron?

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35. What volume of nitric oxide (page 78) will be formed when 5 liters of nitrogen combine with oxygen? Assume constant temperature and pressure.

36. What volume of carbon dioxide results from the complete burning of 25 liters of methane gas? Assume constant temperature and pressure.

37. What volume of carbon dioxide results (standard conditions) from the complete burning of 300 grams of methane gas?

38. How many liters of nitrogen gas at standard conditions are required to form 300 grams of ammonia in a completed reaction?

39. What volume of sulfur dioxide will result, at 30°C. and 750 mm. pressure, when 100 grams of sulfur is burned?

40. Nitrogen gas is formed when nitrous acid acts upon aniline ($\text{C}_6\text{H}_5\text{NH}_2$), according to the following equation.



What volume of nitrogen, measured over water at 24°C. and 763 mm. pressure, could be obtained in this manner from 10.8 g. of aniline? Assume no loss due to solution.

Problems Involving Normality and Molarity. Normality is defined as the number of gram equivalent weights (page 178) of electrolyte per liter of solution, hence for any volume of solution:

(Normality)(Volume in liters) = Number of gram equiv. wts. of solute.

The number of gram equivalent weights, multiplied by the grams in one gram equivalent weight, will be the grams of solute.

(Normality)(Volume in liters)(Gram equivalent weight)
= Grams solute

This is like saying the number of billiard balls in a pile of identical billiard balls, multiplied by the weight in grams of one billiard ball, will be the weight in grams of the pile. The equa-

tion is of value in converting normality to weight of solute and vice versa.

EXAMPLES: 50 grams of potassium hydroxide, KOH, is present in 400 ml. of solution. What is the normality of the solution?

$$\begin{aligned}(\text{Normality})(0.400)(56) &= 50 \\ \text{Normality} &= (50)/(56)(0.400) \\ \text{Normality} &= 2.2\end{aligned}$$

A solution of acetic acid is 0.5274 *N*. What weight of hydrogen acetate (pure acetic acid, HCO_2CH_3) is present in 748.4 ml. of solution?

$$\begin{aligned}(0.5274)(0.7484)(60.05) &= \text{grams acetic acid} \\ &= 23.70 \text{ grams}\end{aligned}$$

Normality is a convenient way to express concentrations because when chemical changes take place between solutions of different electrolytes, equal volumes of solutions of like normality just neutralize or react with one another. In general, the number of gram equivalent weights of reacting electrolytes will be the same, and since each is equal to the product of normality and volume, it follows that $N_1V_1 = N_2V_2$.

EXAMPLE: What volume of 0.1234 *N* sodium hydroxide solution will just react with 36.82 ml. of 0.2694 *N* sulfuric acid solution?

$$\begin{aligned}(0.1234)(V_1) &= (0.2694)(36.82) \\ V_1 &= 80.39 \text{ ml.}\end{aligned}$$

A Warning. It is possible to work certain problems by memorizing a general equation and substituting the numerical values given in the problem, without even knowing the meanings of the terms employed. A student who learns thus is on shaky ground; in the face of a new situation, as a slightly changed test problem, or a question as to the derivation and meaning of the general equation, he is lost. It is apparent, too, that this thought goes far beyond chemistry, or even school work in general, in importance.

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Even the procedure of learning general equations and substituting in them is condemned by some educators, but this is so in keeping with our mental habits that it will probably continue to be widely used. However, the student should strive to think of such general equations fundamentally rather than superficially. Thus, in the normality equation given above:

(Normality) (Liters solution) (Gram equivalent wt.) = Grams solute
the meaning of normality and gram equivalent weight should be clear, whereupon the equation is seen to simplify to

$$\underbrace{\left(\begin{array}{c} \text{Number of gram} \\ \text{equivalent wts.} \\ \text{solute per liter} \\ \text{of solution} \end{array} \right) \left(\begin{array}{c} \text{Liters of} \\ \text{solution} \end{array} \right)}_{\text{Number of gram equiv. wts. in solution in question}} \left(\begin{array}{c} \text{Grams in} \\ \text{one gram} \\ \text{equivalent} \\ \text{weight} \end{array} \right) = \text{Grams solute}$$

It is now seen to be an example of a still more fundamental type:

$$(\text{Number of units A})(\text{Units B per unit A}) = \text{Number of units B}$$

and the normality equation is thus similar in kind to one like:

$$(\text{Number of dollars})(\text{Pennies per dollar}) = \text{Number of pennies}$$

If the student learns in this manner he will be able to reconstruct equations, even though he forgets them, provided he retains the meanings of the terms.

41. What weight of potassium sulfate will be present in 700 ml. of 0.500 normal solution?

42. A solution of hydrogen chloride contains 7.34 grams of the substance in 100 ml. of solution. What is the normality?

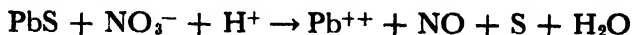
43. A sodium hydroxide solution is 1.23 normal. What volume of this solution will be required to neutralize a liter of a nitric acid solution that is 1.45 normal?

44. What must be the normality of a hydrochloric acid solution if 45.78 ml. of it are required to neutralize 25.11 ml. of 0.2332 *N* potassium hydroxide solution?

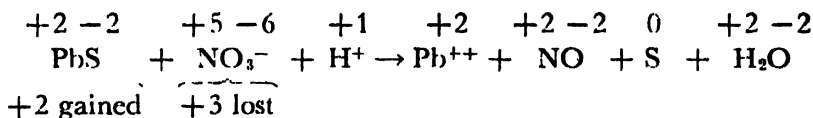
45. A solution of barium hydroxide is 0.318 *N*. 37.83 ml. of this is needed to neutralize a nitric acid solution. What weight

of pure hydrogen nitrate (HNO_3) was present in ionized form in the second solution? What weight of barium nitrate could be recovered by evaporation of the solution left after the titration?

Balancing Oxidation-Reduction Equations. Consider the following equation, which shows the action of dilute nitric acid upon lead sulfide.



While equations of this type can be balanced by trial and error, one is apt to run into difficulties, and a better procedure is to use a method which involves logical steps. In the valence change method described below, the first step is to assume for convenience that each element in the equation has an electrovalence² (which of course it may not); these electrovalences are written over each element.



It is now a simple matter to pick out the elements which have lost and gained in positive valence. The loss or gain can be written below the elements, as shown above. When one becomes experienced in balancing this type of equation, the valences lost and gained can be found without first writing down all valences. When an element is in the *free state* (not ionic), as sulfur in the equation, its electrovalence is called *zero*.

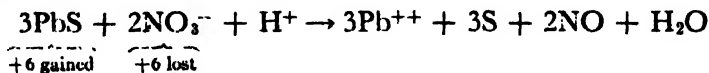
In this example, therefore, sulfur is oxidized, since its valence changes from -2 to zero, and nitrogen is reduced, because its valence changes from $+5$ to $+2$.

The second step is to take enough of the molecules or ions containing these elements so that the total valence change for

² These assumed electrovalences, which are employed as a convenience in the balancing of oxidation-reduction equations, are usually called oxidation numbers or valence numbers. They have some basis of fact, even when they are used for the atoms in covalent molecules such as H_2O , because the electrons in covalent bonds are usually drawn more tightly to one element than to the other, giving a somewhat electrovalent character to the bond.

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the oxidized element is the same as that for the reduced element. This involves finding a least common multiple (six in the example). There must accordingly be three sulfur atoms and two nitrogen atoms in the equation.

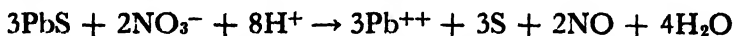


A simple way to arrive at these quantities is to put the valence change for the nitrogen in front of the PbS and the S, and the valence change for the sulfur in front of the NO₃⁻ and the NO. However, equations sometimes result which contain two or three times as much of everything as necessary when this simple transfer of numbers is used.

The third step is to take enough water molecules to balance the oxygen. In the example, four water molecules are needed.



The final step is to include enough hydrogen ions to balance the equation with respect to this element.



The equation is now balanced. As a check, see if the excess of ion charges on the left hand side of the equation is the same in quantity and sign as that on the right hand side. In the example above it is plus six on each side.

In summary, then, the following steps are required in the balancing of an oxidation-reduction equation. (a) Find the elements oxidized and reduced, and the valence change of each. (b) Take enough ions or molecules containing these elements so that the valences lost equal the valences gained. (c) Include enough water to balance the oxygen. (d) Make the number of hydrogen ions sufficient to balance that element. (e) As a check, see that the excess of positive or negative charge on the ions is the same for both sides of the equation.

Oxidation-reduction equations are not always written ionically. The one just balanced might be written:



The balancing technique is nearly the same. (a) The elements oxidized and reduced are found, together with their valence changes. (b) The valences lost are made equal to the valences gained. Thus:



Now the method varies somewhat from the previous one.

(c) When acid radicals are common to both sides of the equation take enough additional acid molecules on the left to supply those radicals needed on the right. In the present equation the nitrate radical is common to both sides. Six *additional* nitric acid molecules are therefore needed on the left to supply the six nitrate radicals on the right.



(d) Include enough water molecules to balance the hydrogen and (e) check the work by counting the oxygen atoms on each side of the equation to see that they balance.



46. Balance the following oxidation-reduction equations.

- (a) $\text{MnO}_4^- + \text{Fe}^{++} + \text{H}^+ \rightarrow \text{Fe}^{+++} + \text{Mn}^{++} + \text{H}_2\text{O}$
- (b) $\text{PbS} + \text{NO}_3^- + \text{H}^+ \rightarrow \text{PbSO}_4 + \text{NO}_2 + \text{H}_2\text{O}$
- (c) $\text{Cr}_2\text{O}_7^{--} + \text{Sn}^{++} + \text{H}^+ \rightarrow \text{Cr}^{+++} + \text{Sn}^{++++} + \text{H}_2\text{O}$
- (d) $\text{Zn} + \text{NO}_3^- + \text{H}^+ \rightarrow \text{Zn}^{++} + \text{NH}_4^+ + \text{H}_2\text{O}$
- (e) $\text{As}_2\text{O}_3 + \text{Zn} + \text{H}^+ \rightarrow \text{AsH}_3 \uparrow + \text{Zn}^{++} + \text{H}_2\text{O}$
- (f) $\text{Fe}(\text{CrO}_2)_2 + \text{NaOH} + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{Na}_2\text{CrO}_4 + \text{H}_2\text{O}$
- (g) $\text{As}_2\text{S}_3 + \text{NO}_3^- + \text{H}^+ \rightarrow \text{AsO}_4^{--} + \text{SO}_4^{--} + \text{NO}_2 + \text{H}_2\text{O}$
- (h) $\text{KIO}_3 + \text{KI} + \text{HCl} \rightarrow \text{KCl} + \text{I}_2 + \text{H}_2\text{O}$
- (i) $\text{Cu} + \text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO}_2 + \text{H}_2\text{O}$

Miscellaneous Problems

47. If 30 milligrams of dry oxygen at 760 mm. pressure can be dissolved by a liter of water, what must be the temperature of the system (graph on page 172)?

48. A specimen of gas with a volume of 23.7 ml. weighs 0.0293 g. The gas pressure is 740 mm., and the temperature is 23°C. What is the density of the gas (weight of a liter at standard conditions)?

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49. A crystal of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (Glauber's salt) weighing 0.5 gram is dropped into a supersaturated solution of that substance. The solution is cooled to 20°C . and allowed to stand until all excess salt has crystallized out, then the crystals are filtered off, dried³ and found to have a weight of 12.4 grams. The filtrate, a saturated solution at 20°C ., is found to weigh 93.7 g. What was the total weight of Glauber's salt in the original supersaturated solution (graph in Figure 8.5, page 174)?

50. The density of tungsten metal is 19.3 grams per cubic centimeter. Calculate the weight in pounds of a cubic foot of tungsten (Appendix H).

51. A solution contains 8.00 per cent of ammonium chloride by weight and has a density of 1.023 grams per cubic centimeter. What is the molarity of the solution?

52. A solution of sulfuric acid is 4.016 *N* and has a density of 1.124 grams per cubic centimeter. What is the percentage by weight of pure hydrogen sulfate present?

³ Surface water removed, not the water of hydration.

ANSWERS TO SUPPLEMENTARY PROBLEMS

- | | |
|--|---|
| <p>(2) 48 g.
 (3) 96 g.
 (4) 366 g.
 (5) 602,300,000,000,000,000,000,000
 (6) 1.3×10^{-4} g.
 (7) 10^6 cc.; 1000 l.
 (8) 7.64×10^{-23} g.
 (9) 227°C., 441°F., 260°C., 533°K.
 (10) 39.34% Na, 60.66% Cl in NaCl
 27.37% Na, 1.20% H, 14.30% C, 57.13% O in NaHCO₃
 8.26% Na, 11.48% O, 69.03% C, 11.23% H in NaO₂C₁₆H₃₁
 (11) (a) 18% H, 82% O; (b) 11% H, 89% O
 (12) 36.08% H₂O in CuSO₄·5H₂O; 72.67% O in Na₂CO₃·10H₂O
 (13) 37.1 ml.
 (14) 475 ml.
 (15) 119.5 ml.
 (16) Yes, to 32.2°C.
 (17) 721 ml.
 (18) 736 mm.
 (19) 51.9 ml.
 (20) 0.21 mile per second
 (21) 2.5 times as fast
 (22) 8.3 mm.
 (23) 64.4%</p> | <p>(24) Dried, since it is almost saturated.
 (25) 15.7°C.
 (26) 16.1
 (27) 1.34 g. per liter
 (28) 28.1
 (29) 0.0545 g.
 (30) 17.032; 82.25%; 0.760 g./l.; 73.7 l.
 (31) 18.8 l.
 (32) 25.8 g.
 (33) 137.2 g.
 (34) 13.82 g.
 (35) 10 l.
 (36) 25 l.
 (37) 419 l.
 (38) 197.2 l.
 (39) 78.6 l.
 (40) 2.90 l.
 (41) 30.49 g.
 (42) 2.01 N.
 (43) 1.18 l.
 (44) 0.1279 N.
 (45) 0.758 g.; 1.57 g.
 (46) Coefficients:
 (a) 1, 5, 8, 5, 1, 4; (b) 1, 8, 8, 1, 8, 4; (c) 1, 3, 14, 2, 3, 7; (d) 4, 1, 10, 4, 1, 3; (e) 1, 6, 12, 2, 6, 3; (f) 4, 16, 7, 2, 8, 8; (g) 1, 28, 16, 2, 3, 28, 8; (h) 1, 5, 6, 6, 3, 3; (i) 1, 4, 1, 2, 2
 (47) 48°C.</p> |
|--|---|

554 Answers to Supplementary Problems

(48) 1.377 g. per liter

(51) 1.53 M.

(49) 26.9 ± 0.2 g.

(52) 17.52%

(50) 1205 lbs.

APPENDIX A

FIRST AID MEASURES FOR ACCIDENTS AND ANTIDOTES OF POISONS¹

By W. F. von Oettingen, M.D., Ph.D.

The following directions are intended as first aid measures for accidents and different forms of poisoning. In laboratories connected with institutions or plants which have first aid stations or emergency hospitals, any injury should be reported immediately. If such facilities are not available, and whenever the case is of a more serious nature, a physician should be summoned at once and, in order to avoid any delay, the items in parentheses should be ready for his use upon his arrival.

TREATMENT OF BURNS

In any case of extensive burns of any degree, call physician.

1. From fire, steam, and hot objects. (a) *First degree (reddening):* Oil dressing or bland ointment; gauze saturated with pure vegetable or mineral oil.

(b) *Second degree (blisters):* Cover blister with sterile gauze saturated with olive oil or some burn ointment; apply oil dressing until the wound is healed.

(c) *Third degree (destruction of tissue):* Cover wound with a sterile dressing and call a physician. (Prepare sterile bandaging material; arrange facilities for sterilizing instruments with boiling water; in case of shock: caffeine sodio-benzoate or salicylate for hypodermic injection; normal saline solution.)

2. From acids (hydrochloric, nitric, phosphoric, and sulfuric acids, and chlorine or bromine). Wash with large quantities of water, then with 5 per cent sodium bicarbonate solution, and apply oil dressing. (In case of extensive and severe burns prepare materials for physician as directed under 1, c.)

¹ Reprinted by permission from Lange's *Handbook of Chemistry*, published by Handbook Publishers, Inc., Sandusky, Ohio.

Burns from **hydrofluoric acid**. Wash burn immediately in cold running water until the white coagulated appearance of the area has been replaced by redness, or for a period of at least 4 to 6 hours. Then apply a freshly prepared 20 per cent suspension of magnesium oxide in glycerol. (Prepare a ten per cent magnesium sulfate solution; material for oil dressing; facilities for the sterilization of instruments with boiling water.)

3. From alkalis: Wash the injury with large quantities of water, and cover the wound with an oil dressing or bland ointment. (In case of extensive burns prepare materials for physician as directed under 1, *c.*)

4. From phenols: Wash liberally with alcohol and then apply an oil dressing. (In case of extensive burns prepare materials for physician as directed under 1, *c.*)

5. Burns of the eye should be flushed first with large quantities of water, and then in case of alkalis with 2 per cent boric acid solution, and in case of acids with 3 per cent sodium bicarbonate solution, after which the eye should be covered with gauze moistened with olive oil.

TREATMENT OF CUTS

Clean the wound mechanically using *sterile* forceps or *sterile* gauze and paint the area *surrounding* the injury with 3.5 per cent tincture of iodine.

If the cut is *small*, scrub with soap and water, cover with sterile gauze and bandage or adhesive tape.

If the cut is *severe* and bleeding freely apply a ligature between the site of the injury and the heart in case the blood is red and the flow intermittent; if the blood is dark and the flow continuous, apply the ligature between the injury and the periphery. Cover the wound with sterile gauze until arrival of the physician. (Prepare sterile bandaging material, facilities for sterilizing instruments with boiling water; and in case of severe hemorrhage several liters of sterilized physiological saline solution (0.9 per cent solution of sodium chloride in water) and caffeine sodio-benzoate for hypodermic injection.)

COLLAPSE

Lay the patient flat on the floor and let him inhale *dilute* vapors of ammonia or smelling salts; stimulate the skin by rubbing with stiff brushes. Administer whiskey or coffee *if patient is able to swallow*. In

case the respiration is shallow or arrested, start artificial respiration preferably with simultaneous administration of oxygen or oxygen-6 per cent carbon dioxide mixture. (Prepare camphor oil, caffeine sodio-benzoate for hypodermic injection, sterilized physiological saline solution (0.9 per cent solution of sodium chloride in water) and a cylinder of oxygen-6 per cent carbon dioxide.)

TREATMENT OF POISONINGS

Call physician. If cause is known, follow immediately the directions given below.

Acids. When taken orally, rinse the mouth with water then with 5 per cent sodium bicarbonate; give milk and a suspension of 10 grams of magnesium oxide (magnesia) in 150 cc of water; or limewater and oil; or a thin flour paste. (Prepare sterilized physiological saline solution as directed under *collapse*, camphor oil and solution of caffeine sodio-benzoate.)

Alcohols. Give large quantities of warm water and if possible gastric lavage, emetics such as mustard water, and coffee. (Prepare caffeine sodio-benzoate, and oxygen-6 per cent carbon dioxide mixture; stomach tube.)

Aldehydes. Give a tumbler full of 0.2 per cent ammonia solution followed within a few minutes by milk. (Prepare stomach tube, caffeine sodio-benzoate, physiological saline solution as directed above, and oxygen.)

Alkaloids. Immediately give one or two tablespoonfuls of purified charcoal in suspension in a glass of water; then give an emetic such as soap water. (Prepare caffeine sodio-benzoate, chloral hydrate, chloroform, and oxygen-6 per cent carbon dioxide mixture.)

Ammonia. Administer large quantities of water containing vinegar or lemon juice and later give olive oil. (Prepare materials as given above for *acids* for use of the physician upon his arrival.) If inhaled, transfer patient to fresh air and keep him at rest.

Aniline. If taken by mouth, give large quantities of soap water, administer oxygen freely, combined with artificial respiration if necessary, saline cathartics, *give no alcohol or oils*. If inhaled, transfer patient to fresh air, let him have absolute rest and let him inhale oxygen.

(Prepare materials as given under *acids*. Keep oxygen or oxygen-6 per cent carbon dioxide mixture ready.)

Arsenic or Antimony. Give an emetic such as soap water and a cathartic such as epsom salts; *do not rely upon chemical antidotes*. (Prepare stomach tube, physiological saline, and caffeine sodio-benzoate.)

Arsine. Absolute rest; free administration of oxygen. (Prepare facilities for sterilizing instruments with boiling water, caffeine sodio-benzoate, and oxygen.)

Barium salts. Give emetics such as soap water, and saline cathartics such as epsom or Glauber's salts. (Prepare stomach tube, and a 25 per cent magnesium sulfate solution for hypodermic injection.)

Benzene. If taken by mouth, give emetics such as soap water or mustard water, cathartics, artificial respiration with simultaneous administration of oxygen, coffee. (Prepare stomach tube, caffeine sodio-benzoate, and oxygen.) If inhaled, transfer patient to fresh air, prevent chilling, let him have absolute rest, if necessary let him inhale oxygen until physician arrives.

Carbolic acid. Give soap water as an emetic, large quantities of water, syrup of lime, or a solution of one part of potassium permanganate in 4000 parts of water. (Prepare stomach tube, caffeine sodio-benzoate, oxygen.)

Carbon monoxide, Ethylene, Acetylene, Illuminating gas. Transfer patient to fresh air, prevent chilling, administer oxygen, if respiration is slow, irregular or intermittent, this should be combined with the administration of oxygen and artificial respiration in case the respiration has stopped. (Prepare caffeine sodio-benzoate, oxygen.)

Chlorine, Bromine. If taken orally, rinse mouth with 3 per cent sodium bicarbonate and magnesium oxide in water; give milk and suspension of 10 g. magnesium oxide in 150 cc. of water. (Make preparations for the arrival of physician as directed under *acids*.) If inhaled, follow the treatment as given under *phosgene*.

Hydrocyanic acid, Cyanides. If taken orally, give a 1 per cent solution of sodium thiosulfate or 0.025 per cent solution of potassium permanganate alkalized with sodium bicarbonate. Give an emetic

such as mustard water or soap water and have patient inhale the contents of one pearl of amyl nitrite. Give artificial respiration with free administration of oxygen. (Prepare caffeine sodio-benzoate, oxygen-6 per cent carbon dioxide mixture, stomach tube, several liters of an aqueous 0.05 per cent potassium permanganate solution.) If inhaled, start with inhalation of one pearl of amyl nitrite and artificial respiration with administration of oxygen.

Hydrogen sulfide. Artificial respiration with simultaneous administration of oxygen. (Prepare oxygen-6 per cent carbon dioxide mixture.)

Iodine. Give an emetic such as soap water; a 1 per cent aqueous solution of sodium thiosulfate (Hypo); starch paste; milk. (Prepare stomach tube and several liters of an aqueous 1 per cent sodium thiosulfate solution.)

Lead compounds. Give large quantities of epsom salt. (Prepare stomach tube.)

Mercury compounds. Immediately give three raw eggs in a quart of milk and an emetic such as soap water. (Prepare stomach tube, hydrogen peroxide, and an hypophosphite-peroxide mixture composed of 1 gram sodium hypophosphite, 5 cc. hydrogen peroxide, and 10 cc. of water for each 0.1 gram of mercuric chloride in the stomach of the patient.)

Morphine alkaloids. Give strong coffee, hot bath, and artificial respiration. (Prepare oxygen-6 per cent carbon dioxide mixture, caffeine sodio-benzoate, 0.1 per cent atropine sulfate solution for hypodermic use, stomach tube, and several liters of a 0.1 per cent solution of potassium permanganate in water.)

Nitric vapors. *Absolute rest!!!*, even in moderate poisoning; inhalation of oxygen. (Prepare caffeine sodio-benzoate, facilities for sterilization of instruments with boiling water, and physiological saline solution as directed under *collapse*.)

Nitro compounds. Give emetic such as mustard water, and saline cathartics; *avoid alcohol, fats, and oil*. (Prepare stomach tube, caffeine sodio-benzoate, and oxygen-6 per cent carbon dioxide mixture.)

Oxalic acid. Give emetic such as mustard water; syrup of lime, lime water; castor oil. (Prepare stomach tube; sterile aqueous 3 per cent solution of calcium lactate or calcium gluconate in ampoules for intravenous injection.)

Permanganate. Give water; emetic such as mustard water; starch paste. (Prepare stomach tube.)

Phosgene. *Absolute rest!!!*, even in moderate cases; inhalation of oxygen. (Prepare caffeine sodio-benzoate, and facilities for sterilization of instruments with boiling water.)

Phosphorus. Give 200 cc. of a 0.2 per cent aqueous solution of copper sulfate. *Avoid fats and oils.* (Prepare stomach tube, several liters of a 0.2 per cent aqueous solution of copper sulfate, a 0.1 per cent aqueous solution of potassium permanganate, liquid petrolatum.)

Pyridine. Give large quantities of tea or coffee; artificial respiration. (Prepare stomach tube, caffeine sodio-benzoate, and oxygen.)

Sodium fluoride, Roach powder insecticide. Give limewater or weak solutions (2 per cent) of calcium chloride. (Prepare for gastric lavage, keep limewater ready, and sterile 1 per cent solution of calcium chloride for intravenous injection, or calcium gluconate for intramuscular injection.)

Silver compounds. Give large quantities of common salt or sodium chloride solution. (Prepare stomach tube.)

Tin compounds. Give emetic such as soap water; milk of magnesia; oils. (Prepare stomach tube, caffeine sodio-benzoate.)

Zinc compounds. Give emetic such as soap water, and an egg in milk. (Prepare stomach tube, caffeine sodio-benzoate.)

APPENDIX B

SATURATION PRESSURES OF WATER VAPOR AT DIFFERENT TEMPERATURES

Temperature	Water Vapor Pressure	Temperature	Water Vapor Pressure
-10°C.	2.149 mm.	24°C.	22.377 mm.
-5	3.163	25	23.756
0	4.579	26	25.209
1	4.926	27	26.739
2	5.294	28	28.349
3	5.685	29	30.043
4	6.101	30	31.824
5	6.543	31	33.695
6	7.013	32	35.663
7	7.513	33	37.729
8	8.045	34	39.898
9	8.609	35	42.175
10	9.209	36	44.563
11	9.844	37	47.067
12	10.518	38	49.692
13	11.231	39	52.442
14	11.987	40	55.324
15	12.788	45	71.88
16	13.634	50	92.51
17	14.530	55	118.04
18	15.477	60	149.38
19	16.477	70	233.7
20	17.535	80	355.1
21	18.650	90	525.76
22	19.827	100	760.00
23	21.068	110	1074.6

APPENDIX C

COMMON ALLOYS

Name	Component		
	Major	Intermediate	Minor
Babbitt metal	Sn (90)		Sb (7), Cu (3)
Battery plate	Pb (94)		Sb (6)
Brass, red	Cu (85-90)	Zn (10-15)	
Brass, yellow	Cu (67)	Zn (33)	
Bronze	Cu	Sn	± Zn, P
Coinage, gold	Au (90)	Cu (10)	
Coinage, nickel	Cu (75)	Ni (25)	
Coinage, silver	Ag (90)	Cu (10)	
Dental amalgam	Hg (70)	Cu (30)	
Dental gold	Au		Ag, Cu
Duralumin	Al		Cu, Mn, Mg
German silver	Cu (55)	Zn (25), Ni (20)	
Invar	Fe (63.8)	Ni (36)	C (0.2)
Magnalium	Al	Mg	
Monel metal	Ni	Cu	Fe, Mn, Si, C
Nichrome	Ni	Fe, Cr	C
Lead for shot	Pb (99.8)		As (0.2)
Pewter	Sn		Cu, Bi, Sb
Steel	Fe		C
Steel, stainless	Fe	Cr	C, ± Ni, Cu, Mn, Mo
White gold	Au (90)	Pd (10)	

APPENDIX D

COLORS AND PRECIPITATES IN NATURAL WATERS

Condition	Probable Cause
Formation of white precipitate when water is heated	Water contains calcium and/or magnesium bicarbonates which decompose when heated to form carbonate precipitates
Milky water, slowly clearing	Entrained air
Clear well water turning white, then reddish, then forming red deposit	Ferrous iron salts in the water. These oxidize and hydrolyze to ferric hydroxide
Clear well water turning mahogany colored	Manganese salts present. These may also cause dark-colored precipitates
Slowly settling reddish material in surface water	Iron bacteria
Brown surface water, acid in character	Swampy water containing organic matter. Characteristic of cedar swamps
Green growths in surface water	Algae
Dusty material on surface of water	Pollen

APPENDIX E

CHEMICAL COMPOSITION OF FAMILIAR MATERIALS

Name	Chemical Composition
Agate	Silicon dioxide, SiO_2
Alcohol	Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$
Alum	Hydrated potassium aluminum sulfate, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
Aspirin	Acetyl salicylic acid, $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$
Atabrine	Quinacrine hydrochloride, $\text{C}_{23}\text{H}_{30}\text{ON}_3\text{Cl} \cdot 2\text{HCl}$
Bakelite	Plastic containing (if dark colored) phenol formaldehyde resin
Baking soda	Sodium bicarbonate, NaHCO_3
Bentonite	Impure aluminum silicate
Benzine	Gasoline
Bleaching powder	Impure $\text{CaCl}(\text{OCl})$
Borax	Hydrated sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Bluing	$\text{FeKFe}(\text{CN})_6$ in aqueous suspension
Brimstone	Sulfur
Calgon	Sodium phosphate glass, $1 \cdot 1\text{Na}_2\text{O} \cdot 1\text{P}_2\text{O}_5$
Calomel	Mercurous chloride, Hg_2Cl_2
Carbolic acid	Phenol, $\text{C}_6\text{H}_5\text{OH}$
Caustic soda	Sodium hydroxide, NaOH
Cellophane	Regenerated cellulose
Chalk	Usually calcium carbonate, CaCO_3
Clay	Impure aluminum silicate
Coal gas	Chiefly methane, CH_4 , and hydrogen
Corrosive sublimate	Mercuric chloride, HgCl_2
Chrome green	Chromic oxide, Cr_2O_3
Chrome yellow	Lead chromate, PbCrO_4
DDT	Dichlorodiphenyltrichloroethane

Name	Chemical Composition
Dextrose	Glucose, $C_6H_{12}O_6$
Diatomaceous Earth	Chiefly silicon dioxide
Ether	Diethyl ether, $(C_2H_5)_2O$
Flint	Silicon dioxide, SiO_2
Fool's Gold	Iron disulfide, FeS_2
Formalin	Water solution of formaldehyde, CH_2O
Fuller's Earth	Hydrated aluminum and magnesium silicates
Fusel oil	Mixed amyl alcohols
Gasoline	Hydrocarbon mixture averaging about C_7H_{16}
Grain alcohol	Ethyl alcohol, C_2H_5OH
Grape sugar	Glucose, $C_6H_{12}O_6$
Gun cotton	Nitrated cellulose
Gypsum	Hydrated calcium sulfate, $CuSO_4 \cdot 2H_2O$
Hypo	Hydrated sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$
Invert sugar	Mixture of glucose and fructose obtained from sucrose
Javelle water	Solution of sodium hypochlorite, $NaOCl$
Lampblack	Chiefly carbon
Lanolin	Wool grease. Largely fatty acid esters of cholesterol
Laughing gas	Nitrous oxide, N_2O
Linewater	Solution of calcium hydroxide
Litharge	Plumbous oxide, PbO
Lunar caustic	Silver nitrate, $AgNO_3$
Lye	Sodium hydroxide, $NaOH$
Lysol	Solution of cresols in aqueous soap solution
Marble	Calcium carbonate, $CaCO_3$
Milk of lime	Suspension of calcium hydroxide in water
Milk of magnesia	Suspension of magnesium hydroxide in water
Moth balls	Naphthalene, $C_{10}H_8$
Moth crystals	<i>p</i> -Dichlorobenzene, $C_6H_4Cl_2$
Muriatic acid	Water solution of hydrogen chloride, HCl , hydrochloric acid
Oil of wintergreen	Methyl salicylate
Permutit	Synthetic hydrated aluminum silicate containing replaceable sodium ions

Name	Chemical Composition
Petrol	Gasoline
Petroleum naphtha	Petroleum hydrocarbon mixture boiling from 95°–100°C.
Plaster of Paris	Partially hydrated calcium sulfate, $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$
Producer gas	Chiefly carbon monoxide and nitrogen
Prussic acid	Hydrocyanic acid, HCN
Quartz	Crystalline silicon dioxide, SiO_2
Quicksilver	Mercury
Rayon	Regenerated cellulose
Red lead	Lead orthoplumbate, Pb_3O_4
Rock salt	Sodium chloride, NaCl
Rouge	Ferric oxide, Fe_2O_3
Sal ammoniac	Ammonium chloride, NH_4Cl
Saltpeter	Niter, potassium nitrate, KNO_3
Silica	Silicon dioxide, SiO_2
Soda ash	Impure sodium carbonate, Na_2CO_3
Solvent naphtha	Coal tar distillate, boiling from 80°–110°C.
Styron	Polystyrene
Sugar	Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
TNT	Trinitrotoluene, $\text{CH}_3\text{C}_6\text{H}_2(\text{NO}_2)_3$
2,4-D	2,4-dichlorophenoxyacetic acid
Verdigris	Basic copper acetate, $\text{Cu}(\text{OH})\text{C}_2\text{H}_3\text{O}_2$, also basic copper carbonate
Washing soda	Hydrated sodium carbonate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Water gas	Mixture of carbon monoxide and hydrogen
White lead	Basic lead carbonate
Water glass	Water solution of sodium silicate
Wood alcohol	Methyl alcohol, CH_3OH

APPENDIX F

CHEMICAL COMPOSITION OF GEM MINERALS

Name	Composition
Alexandrite	See Chrysoberyl
Amber	Fossilized resin
Amethyst	Silicon dioxide plus manganese compounds
Aquamarine	See Beryl
Beryl	Beryllium aluminum silicate, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$
Chrysoberyl	Beryllium aluminate, $\text{BeO} \cdot \text{Al}_2\text{O}_3$
Chrysolite	Magnesium iron silicate
Diamond	Carbon
Emerald	Beryl plus chromium compounds
Garnet	$\text{A}_3\text{B}_2(\text{SiO}_4)_3$, where A is Ca, Mg, or ferrous iron and B is Al, Cr, or ferric iron
Jade	Mixture of silicates, usually Mg, Ca or Al, Na
Lapis lazuli	Complex mixture, chiefly lazurite, $3\text{NaAlSiO}_4 \cdot \text{Na}_2\text{S}$
Moissanite	Silicon carbide, SiC
Opal	Hydrous silica
Ruby	Aluminum oxide plus small amounts of chromium compounds
Sapphire	Aluminum oxide, Al_2O_3
Titanite	Calcium silicotitanite, $\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$
Topaz, true	Basic aluminum fluosilicate, $\text{Al}_2(\text{F}, \text{OH})_2\text{SiO}_4$
Topaz, oriental, sinoky, Spanish, etc.	Quartz plus impurities
Tourmaline	Complex aluminum borosilicate, usually with small amounts of other metal ions
Turquoise	Basic copper aluminum phosphate, $3\text{Al}_2\text{O}_3 \cdot \text{CuO} \cdot 2\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$
Zircon	$\text{ZrO}_2 \cdot \text{SiO}_2$

APPENDIX G

STAIN AND SPOT REMOVAL¹

General Precautions. (a) Remove spots and stains promptly, as they may become permanently set after a lapse of time. (b) Avoid heat, since this may bring about chemical changes which will set the stain. (c) Pat with a cloth pad wet with the spotting reagent, rather than rub. Rubbing itself may make a noticeable spot because of frictional damage to cloth or color. (d) Test reagents to be used on an unexposed seam to note whether the color of the cloth will be affected. (e) Avoid using chlorine bleach (sodium hypochlorite solution) on silk or wool. (f) Do not allow perfume, cologne, deodorants, antiperspirants, nail polish, or polish remover to get on garments. Solvent or chemical action of these may injure the cloth or cause bleeding of dyes.

Reagents for Stain Removal in the Home: water, carbon tetrachloride, dilute ammonia solution, acetic acid (white vinegar), glycerine, sodium hypochlorite (bleaching) solution.

Oil and Fat Stains. Carbon tetrachloride is an effective oil and fat remover if used promptly. Avoid prolonged breathing of the vapor of this solvent.

Paint Spots. Carbon tetrachloride will remove most of such spots, but is not effective for some pigments. The writer has found that lard, or synthetic cooking fats, worked into the cloth is effective in removing paint spots, including the pigment. The fat can then be removed with carbon tetrachloride.

Beverage Stains (coffee, tea, fruit or vegetable juices, alcoholic liquors). Sponge the stain out *promptly* with water. Avoid use of soap or heat. Twenty per cent glycerine solution or white vinegar may help if water fails to remove stain.

Milk Stain. Wash promptly with water. If this is not effective, let garment dry, take out butter fat with carbon tetrachloride, then use ammonia or soap solution to take out casein residue.

¹ This section summarizes information received from the National Institute of Cleaning and Dyeing, Silver Springs, Md.

Iodine Stains. Dilute ammonia solution.

Ink Stains. This is a difficult subject on which to give advice, since there are more than 200 different kinds of ink. Do not use milk. Equal parts of glycerine and water may be effective in removing dye inks. Dilute sodium hypochlorite (bleaching) solution containing a little vinegar may be applied for a short time to cotton and linen fabrics for the removal of ink and other color stains, but it may also remove original cloth color. Cloth should be thoroughly rinsed after short use of this mixture. This mixture will quickly damage silk or wool, but if a garment is useless because of such a stain which can neither be removed at home nor by the drycleaner, the reader may wish to try it with caution.

APPENDIX H

CONVERSION FACTORS

To Convert	To	Multiply By
Centimeters	Feet	0.032808
Cubic Centimeters	Quarts	0.0010567
Feet	Centimeters	30.480
Grams	Pounds	0.0022046
Milliliters	Quarts	0.0010567
Pounds	Grams	453.59
Quarts	Cubic Centimeters	946.36
Quarts	Milliliters	946.33

APPENDIX I

Four-Place Logarithms of Numbers

Natural numbers	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6171	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	3	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Four-Place Logarithms of Numbers.—(Continued)

Natural numbers	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7635	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4

Antilogarithms to Four Places

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	2	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	2	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	2	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	2	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	2	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	2	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	1	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	3
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	3	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	4	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	6
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	2	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	2	3	4	4	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	3	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

Antilogarithms to Four Places — (Continued)

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	5	6	7	
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	1	2	3	4	5	6	7	
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	1	2	3	4	5	6	7	
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	7	
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	7	
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	2	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	3	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	7	8	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	5	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	3	5	6	7	8	9	10
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	7	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	11	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	7	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	14	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	4	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	6	7	9	11	13	15	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	9	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	6	9	11	13	15	17	19
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	21

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